Material development for India's nuclear power programme

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Abstract. The area of materials research has registered a phenomenal growth in the recent years, assiduously accepting and assimilating ideas, concepts and analytical as well as experimental methodologies and techniques form almost all scientific disciplines, thereby demonstrating its remarkably multidisciplinary and interdisciplinary character. The focus of the materials programme of this centre is to provide materials, processes and processing solutions to the emerging needs of evolving indigenous nuclear energy systems by proactive research and development on a continuing basis. The initial stage of our activities was formulated around three stage Indian nuclear power programme. In stage I, material issues related to in-core materials with emphasis on development of fabrication routes of zirconium alloys for structural application were addressed. Subsequently the thrust areas were development and characterization of mixed oxide fuel, advanced zirconium alloys, structural steels, superalloys, neutron absorber materials based on boron carbides and borides, and shape memory alloys. The research was useful for in-service performance evaluation, safety assessment, residual life estimation and life extension of nuclear reactors built during stage I i.e., PHWRs and BWRs. It also included developments which would permit rapid expansion of nuclear power initially through fast breeder reactor based on mixed oxide fuel and later based on metallic fuels. For the 3rd stage, multi-layer coatings, graphite coolant tube, BeO, refractory metals and alloys, heat-treated zirconium alloys are being developed for CHTR, ADSS and AHWR. The materials being developed for fusion programme are low Z and high Z material for plasma facing application, Cu-alloys for heat sink, austenitic steels, RAFMS and ODS for structurals and NbTi, Nb_3Sn and Nb_3Al superconductors, lithium titanate, lithium silicate breeders, and Pb–Bi coolant. A brief overview of the materials research activities currently being pursued at Bhabha Atomic Research Centre is presented in this article.

Keywords. Nuclear materials; 3-stage power programme; reactor systems; Zr-alloys; hydride embrittlement; structural steels.

1. Introduction

As our country has posted nearly double digit growth in gross domestic product in percentage terms over the last decade and continuous effort is being made to sustain it in future, major

expansion in power generation capacity is underway. Though fossil fuel is going to be the mainstay of our energy source for quite some time, considering our dependence on the imported oil, political instability in the major oil producing countries, large distance of the industrialized states from the coalfields, requirement of constructing large dams/reservoirs for setting up of hydel power plants necessitating displacement of large population, technological challenge in harnessing solar power, it is imperative to consider all the options available to us to achieve energy security and to provide decent standard of life to all strata of the society. Indeed nuclear power is going to play a significant role not only in terms of quantum of power generated but also in terms of variation in types of reactors to be deployed (Glasstone & Sesonske 1988). Pressurized Heavy Water Reactor (PHWR) has been our mainstay in our nuclear power generation strategy so far. As we are poised for major expansion in nuclear power generation capacity, apart from PHWRs a large number of light water reactors and fast breeder reactor are expected to be deployed. In addition to this, Advanced Heavy Water Reactor (AHWR), Compact High Temperature Reactor (CHTR) and Accelerator Driven Sub-critical Systems (ADSS) and Fusion systems (Kakodkar 2007) are being developed. This throws up new challenges in terms of development of zirconium alloy pressure tube having enhanced resistance to in-reactor dimensional changes, zirconium alloy claddings capable of withstanding significantly large burn-ups, pressure vessel steels for light water reactors, ferritic and austenitic steels for fast breeder reactors and structural and functional materials for new reactor systems.

The science and engineering of nuclear reactor systems has come to a point where it is no more the design, engineering or technology but the problems associated with the materials used in its construction and societal acceptance that have become the limiting factor for its progress. Over the next few decades, the progress made in the operation of existing nuclear power plants and construction of new nuclear reactors will depend on how well the performance of the existing materials can be understood and improved under the normal and extreme conditions prevailing within a reactor and how effectively the perception of societal concern regarding its safety can be addressed. The safe operation of a reactor during its lifetime depends on the proper site selection for the reactor, meeting stringent requirement during its construction, quality assurance during the fabrication of its components and capability to predict the degradation of components during service.

The mission of Materials Group, BARC is to provide materials, processes and processing solutions to the emerging needs of evolving indigenous nuclear energy systems by proactive research and development on a continuing basis. To address this mandate various activities are being pursued, including the development and characterization of mixed oxide fuel, advanced zirconium alloys, structural steels, superalloys, neutron absorber materials based on boron carbides and borides, shape memory alloys, multi-layer coatings, graphite coolant tube, BeO, refractory metals and alloys, heat-treated zirconium alloys for CHTR, ADSS and AHWR. In addition, materials like low Z and high Z material for plasma facing application, Cu-alloys for heat sink, austenitic steels, RAFMS and ODS for structurals and NbTi, Nb_3Sn and Nb_3Al superconductors, lithium titanate, lithium silicate breeders, and Pb–Bi coolant are being developed for fusion programme. The results of these investigations are being published in peer reviewed journals, reports and presented in national and international symposia. As it is not possible to cover the entire spectrum of activities in a single article, it has been decided to describe a selected few activities. This article focuses on the development of zirconium alloy components and its in-service degradation, development of control rod materials, development and characterization of structural steels and functional materials for Indian nuclear power programme.

2. Reactor systems

In a fossil fuel-based power plant the chemical energy released as a result of combustion produces steam in a steam generator, which is used to drive turbine for generating electricity. Nuclear reactor harnesses heat energy released from nuclear fission/fusion for generating steam for running the turbine (Glasstone & Sesonske 1988). High Z elements release energy during fission of its nuclei while low Z isotopes release energy when their nuclei fuse together. Nuclear reactor systems based on fission are already being exploited commercially while those based on fusion are still under development.

Though fission of any transuranic nuclei will produce energy, in order to sustain nuclear fission chain reaction sufficient number of neutrons are also required to be produced during fission. Fission of only three nuclei, viz., U^{233}, U^{235} and Pu^{239}, produce enough neutrons to sustain the chain reaction. These isotopes are called fissile isotopes and are used as fuel in a nuclear reactor. In addition, part of the neutrons produced during fission of fissile isotopes in excess of those required for sustaining the chain reaction can also be used to produce fissile isotope from isotopes like U^{238} or Th^{232}. The latter are called fertile isotopes and are used for breeding fissile isotopes. A suitable coolant is required to extract heat energy from the fuel. However, fuel may react with coolant and hence the fuel is not allowed to come in direct contact with the coolant. Neutron absorbing materials are used as control rods for controlling neutron population inside the reactor (Glasstone & Sesonske 1988).

Based on the neutron energy used to carry out fission reaction, power reactors based on nuclear fission are classified as thermal (neutron energy ~ 0.025 eV) and fast (neutron energy >100 keV) power reactors (Glasstone & Sesonske 1988). Thermal reactors are mostly water cooled while fast reactors are cooled by liquid metal. Apart from coolant low Z elements called moderators are also required to slow down the neutrons produced during fission in a thermal reactor. Different reactors systems are described below briefly.

2.1 *Water cooled reactors*

There are three types of water cooled nuclear reactors, viz., Pressurized Water Reactor (PWR), Boiling Water Reactor (BWR) and Pressurized Heavy Water Reactor (PHWR) (Glasstone & Sesonske 1988). Globally PWR is more popular followed by BWR and PHWR. Both PWR and BWR are pressure vessel type reactor using slightly enriched fuel. The core of the reactor is filled with light water, which acts as coolant as well as moderator. The heat generated by core in these reactors is removed by coolant water flowing directly in contact with fuel rods. In order to avoid boiling of water, the coolant is pressurized. The main difference between a BWR and PWR is that in a BWR, the reactor core heats water, which turns to steam and then drives a steam turbine. In a PWR, the reactor core heats water circulating in the primary heat transport loop, which produces steam in a steam generator and drives the turbine. However, the primary heat transport loop operates at relatively higher pressure and higher temperature in PWR as compared to BWR (table 1).

In PHWR pressure tubes instead of pressure vessels are used to contain the hot pressurized coolant and there is separate coolant and moderator loop. It is cooled and moderated by heavy water and uses natural UO_2 as fuel. Inside pressure tubes coolant heavy water flows under a pressure of ~ 10 MPa and at a temperature of ~ 573 K. Calandria tubes (CT) surrounds the pressure tubes from outside. Garter springs (GS) are provided at regular interval in the annular space to support pressure tube and prevent it from contacting the calandria tube which is surrounded by

Table 1. Salient features of water cooled reactors.

Features	Reactor type		
	PWR	BWR	PHWR
Fuel	Enriched ($\sim$3%) UO_2	Enriched ($\sim$2%) UO_2	Natural UO_2
Coolant	Light water	Light water	Heavy water
Moderator	Light water	Light water	Heavy water
Pressure vessel/tube type	Pressure vessel	Pressure vessel	Pressure tubes
Coolant and moderator loop	same	same	separate
Steam generator	Yes	No	Yes
Pressure boundary material	Pressure vessel steel	Pressure vessel steel	Zircaloy-2 (formerly) Zr-2.5 Nb alloy (currently)
Cladding material	Zircaloy-2, Zircaloy-4 and Zr-1Nb alloy	Zircaloy-2 and Zircaloy-4	Zircaloy-2 and Zircaloy-4
Operating temperature, °C	325	285	293
Operating pressure, MPa	15	7	10
Average burnup, MWd/ton of U	$\sim$50,000	$\sim$30,000	7,000
Rated Power capacity In India, MWe	1000 (VVER)	200 (TAPS)	220 and 540

low pressure, low temperature heavy water moderator contained in a large stainless steel vessel called calandria vessel. A continuous flow of dry carbon dioxide gas is maintained in the annular space between the pressure tube and calandria tube to insulate hot coolant from the moderator. Salient features of the water cooled reactor are summarized in table 1.

Apart from PWR, BWR, PHWR, which form the mainstream for power production at present, advanced versions of PWR, BWR and Advanced HWR (AHWR) are also being considered for launching in near future. The main driving force for development of the advanced version of these reactors is to reduce per unit cost of electricity generated and enhance the safety features, which is being achieved by going for modular design, setting up of cluster power plants, reducing the construction time and cost, and increasing the burnup of the fuel. The targeted burnup for advanced PWR is $\sim$70,000 compared to the present value of $\sim$50,000 while the same for advanced BWRs is $\sim$50,000 and $\sim$30,000 MWd/tone of uranium, respectively. For PHWRs efforts are on to increase the burnup from 7,000 to 20,000 MWd/tone of uranium through use of mixed oxide fuel. AHWR is an Indian design of a thermal breeder reactor having advanced safety features; and is a challenge in material selection for its hundred year design life (Kakodkar 2007).

2.2 *Fast breeder reactor*

The Fast reactors have no moderator and the volumetric energy generation rate by the core is very high; hence for effective cooling, liquid sodium is used as coolant (Kakodkar 2007). As the boiling point of sodium is quite high ($\sim$850°C) at the atmospheric pressure, there is no need to pressurize the coolant; hence a tank containing the core having Pu^{239} based mixed oxide as fuel is submerged in pool of liquid sodium. The heat energy from the liquid sodium in the tank is removed by a primary liquid sodium cooling loop, which dumps its energy to the intermediate liquid sodium cooling loop. The heat energy from the intermediate sodium

cooling loop is used to produce steam for driving turbine. Fast Breeder Test Reactor (FBTR) in operation since more than twenty years at Kalpakkam, Tamilnadu has been used to develop and qualify the technology for 500 MWe Prototype Fast Breeder Reactors (PFBR). Two units of PFBR are expected to be constructed at the same site and four more units are planned. With commencement of power production through PFBR we will be entering in to second stage of the 3 stage nuclear power programme. As the name suggests PFBRs are breeder reactor. This means that these reactors apart from producing electricity will be producing fissile isotopes Pu^{239} and U^{233} from the transmutation of U^{238} and Th^{232} respectively, which are used as blanket materials in the PFBR. U^{233} produced as transmutation product in PFBRs can be used in 3rd stage of the nuclear power programme, which envisages design and construction of thermal breeder reactor. However, to achieve this battery of PFBRs will be required to produce enough fissile material to provide fuel for the thermal breeder reactors to be set up in 3rd stage. Thermal breeder reactors will produce U^{233} from Th^{232} by transmutation apart from producing electricity. Exploitation of vast reserve of Thorium is expected to provide sustainable and viable energy source for few hundred years thereby providing energy security to the country.

2.3 *Fusion reactor*

Fusion reactors aim to exploit energy released during a fusion of low Z nuclei (Kakodkar 2007). It is a clean and inexhaustible source of alternative energy with high environmental safety. However, two major challenges need to be overcome for commercial exploitation of fusion energy. The first one is sustaining the plasma and second is the development the materials capable of performing under fusion reactor environment. Basic physics experiments carried out over the last few decades have demonstrated the possibility of sustaining the plasma for reasonable time under high magnetic fields produced by superconducting magnets. However, engineering feasibility of exploiting fusion energy is yet to be established. The International Thermonuclear Experimental Reactor (ITER) coming up at Cadarache, France is the joint effort of the global community in this direction. The ITER project is aimed to test the engineering feasibility of exploiting fusion for commercial purposes. Though the major part of ITER is for carrying out physics related experiments, three ports have been provided for conducting experiments related to tritium breeding, its recovery, neutronics, Helium/hydrogen embrittlement of structurals, irradiation damage of materials, compatibility of various materials used and joining technologies.

Thus a typical Nuclear Power Plant may use nuclear fuel, coolant, control rod materials, moderators, breeders and structural materials for the major components. During service these materials degrade under the operating condition prevailing in a reactor comprising of radiation, stress, temperature and corrosive environment. Apart from this some of the components also undergo dimensional changes due to creep, radiation induced growth and swelling. The major challenge lies in mitigating the degradation or by developing tools with predictive capability so as to assess the life of the components. Obviously different strategy has to be adopted for different reactor systems.

3. Development of zirconium alloys

The use of natural UO_2 as fuel in PHWRs and slightly enriched fuel in BWRs and PWRs demands that the core structural materials such as cladding tubes (also called fuel tubes), pressure tubes (coolant tubes), calandria tubes, guide tubes and garter springs must have low neutron absorption cross-section and should satisfy the physical, mechanical, metallurgical

and chemical requirements in radiation environment (Dietz 1994). Out of all the elements (http://www.webelements.com) in the periodic table, only four elements satisfy the condition of low neutron absorption to be suitable as base material. These are aluminum, beryllium, magnesium and zirconium. Out of these, beryllium being brittle and chemically toxic can be used only on a limited scale. Magnesium is ruled out in water-cooled reactor because of its high chemical reactivity (Neite *et al* 1996). Because of its low melting point use of aluminum is limited to research reactors only (Murakami 1996). Hence, for water cooled reactors, nature has provided us with the unique but sufficient choice in the form of zirconium based alloys (Lemaignan & Motta 1994; Banerjee *et al* 2002). However, use of zirconium in nuclear reactor is not free of problems and poses several challenges to material scientists and engineers. Zirconium is associated with chemically similar hafnium having high neutron cross-section, which renders it unfit for use in a nuclear reactor. Production of Hf-free nuclear grade zirconium requires special technologies, which has been mastered by only few countries including India in the world. Zirconium is crystallographically anisotropic, as a result, hot worked products of zirconium exhibit anisotropy in mechanical properties. It has limited solid solubility for alloying additions thereby having limited possibility of enhancing mechanical properties by alloying. The anisotropic thermal expansion coefficient poses problems for zirconium alloy components during service at high temperature especially for long products. It is susceptible to aqueous corrosion and dimensional changes under irradiation, and embrittlement due to formation of hydrides and irradiation. These challenges have been overcome to a great extent through technological development in zirconium extraction, modifying manufacturing practice for fabrication of different types of zirconium alloy components, developing life monitoring, life management tools and mechanistic modelling having predictive capability. In this section, production of nuclear grade zirconium metal, development of zirconium alloys, zirconium alloy components used in water cooled reactors, in-service degradation mechanisms of zirconium alloy components and mitigation of present concerns are described briefly.

3.1 *Production of zirconium metal*

Zirconium was first obtained in an elemental form in 1824. Relatively pure metal was produced in 1914 and a high purity sample was made in 1924. The last mentioned sample was obtained by the van Arkel-de Boer process, also known as the iodide process. This process, to date, remains the process for producing fairly large quantities of ultrapure zirconium metal (Ampian 1975). Stringent purity requirements with respect to certain elements has been a key consideration governing the extraction processes for zirconium. The process metallurgy of zirconium presents a variety of technological challenges all along the route the metal traverses from its state of natural dissemination in the earth's crust to its state of ultrapurity for several end use requirements (Krishnamurthy & Sundaram 1978).

Zircon ($ZrSiO_4$) is the only commercially relevant zirconium mineral. It occurs in plenty in the beach sand deposits in various parts of the world and is almost always recovered in beach sands minerals processing as a by-product of the titanium minerals ilmenite and rutile. In India, there are vast deposits of zircon in the coastal beach sands of Kerala, Tamil Nadu and Orissa where it occurs to the extent of 5–9% along with many other valuable minerals. Besides zirconium, zircon contains 2–2.5% hafnium, which is altogether similar to zirconium in its chemical behaviour. Hafnium would thus track zirconium all through the processing flowsheet and would remain in zirconium which could be otherwise ultrapure. For majority of its applications, the presence of hafnium in zirconium is not deleterious but for applications of zirconium in the reactor core, the presence of hafnium is unacceptable (Krishnamurthy & Sundaram 1978).

The cross section for the capture of thermal neutrons is 0.18 barns/atom for zirconium and 105 barns/atom for hafnium. While pure zirconium is essentially transparent to thermal neutrons, metal containing 2% hafnium has a cross section of more than 2 barns/atom. Such a material would seriously interfere with the functioning of the nuclear reactor. Hafnium content of zirconium for reactor core (nuclear grade) should be less than 100 ppm. In the extractive metallurgy of zirconium, separation from hafnium to such levels is one of the most important and difficult steps.

In the flowsheet for the processing of zircon to nuclear grade zirconium metal, there are multiple processes available for every unit operation starting from opening up of the mineral zircon. The choice of the process depends on many factors, the most important being the intended end use of the zirconium values: zirconia ceramics, zirconium alloys for the chemical industry or zirconium alloys for the nuclear reactor core. In the Indian practice for the production of nuclear grade zirconium, caustic fusion process was chosen for treating the mineral. The fused mass is leached and zirconium values (along with hafnium) are obtained in a nitrate liquor.

A number of processes have been suggested for the separation of hafnium and zirconium (Krishnamurthy & Sundaram 1978; Sathiyamoorthy *et al* 1998). These include solvent extraction, ion exchange, distillation, selective partial reduction, vapour phase dechlorination and fractional crystallization/precipitation. Amongst these solvent, extraction has been preferred for industrial practice for many technological and commercial reasons. Even in solvent extraction, there are many choices. In the original method, crude $ZrCl_4(HfCl_4)$ obtained by direct carbo-chlorination of zircon at around 1150°C is dissolved in hydrochloric acid containing ammonium thiocyanate and fed to the extraction system. On contacting with the solvent, Methyl Isobutyl Ketone (MIBK), hafnium thiocyanate dissolves preferentially into it. Zirconium remains in the aqueous phase. Both zirconium and hafnium, now separated, are independently recovered. In the Indian practice, the substantial operating experience of TBP solvent extraction plants in uranium processing, made it easier to choose a TBP system also for zirconium–hafnium separation. The process is based on zirconium extraction from a nitrate feed solution. Hafnium remains in the aqueous phase (raffinate). In the Japanese practice, a sulphate aqueous solution and tri-iso-octyl-amine solvent is used to extract zirconium from the solution and achieve zirconium–hafnium separation.

Pure zirconium solution is obtained after aqueous stripping, and ammonia addition precipitates the hydroxide. This is filtered using rotary drum filters and dried in specially designed ovens in a current of air and finally calcined at 850°C in a rotary furnace to yield the oxide.

Much of the process cost in the production of zirconium is accounted for by the zirconium–hafnium separation step and any process improvement or change at this stage would bring in cost benefits. Zirconium metal is finally produced by Kroll reduction of zirconium tetrachloride. This chloride is obtained by chlorination of zirconium dioxide. This oxide is the product of the solvent extraction separation operation of the leach liquor obtained by soda fusion of zircon mineral. So there is a intermingling of pyro and hydro metallurgical steps in the flowsheet and that means, in the plant practice, considerable cost consequences. A mature process will remove hafnium chloride from the mixed zirconium tetrachloride–hafnium tetrachloride product of zircon chlorination, and the separated pure zirconium tetrachloride would undergo Kroll reduction to nuclear grade zirconium sponge. This process is not only elegant and economical but also environment friendly. Numerous chemical waste streams are avoided and a severely curtailed energy need resulting from decrease in process steps and virtual elimination of avoidable state and phase changes, render the process economical also. The conceptual elegance of this process found expression in what is known as the pyrochemical route for zirconium–hafnium separation.

This process, commercial in France, is considered for use in our country also (Sathiyamoorthy *et al* 1998).

The overall scheme for the pyrochemical separation of zirconium comprises of (i) direct chlorination of zircon sand, (ii) purification of the crude zirconium tetrachloride–hafnium tetrachloride mixture by fused salt scrubbing, (iii) extractive distillation of the purified chloride mixture to separate hafnium tetrachloride from zirconium tetrachloride. Among these steps, the most important is the extractive distillation. Extractive distillation, in principle, is a technique by which the relative volatility of a component is altered by adding a 'solvent'. This alteration in the volatility of the components is desired in view of the very similar volatilities of the zirconium and hafnium tetrachlorides. The solvent in this case is molten $KCl–AlCl_3$ and this molten salt preferentially absorbs zirconium tetrachloride. At BARC, investigations were carried out on a 12 stage 100 mm sieve plate extractive distillation column and the experimental findings revealed the feasibility of separation of hafnium tetrachloride.

The chlorides of many metals are easily produced from their oxides. Usually the chlorides are highly volatile and can be isolated in high purity by simple procedures. They are also readily reducible to metals. In fact, the formation of a metal chloride as an inter-process intermediate and its reduction to metal is a powerful tool for the preparation of pure zirconium and also many other rare metals. This route is usually available when the rare metal oxide is so stable that it cannot be easily or conveniently converted to the metal.

One of the most impressive examples on the success of chloride metallurgy is the extraction of zirconium. The large scale production of zirconium metal would not have been possible or would have been at best very expensive but for the discovery of the Kroll process. Kroll discovered that zirconium tetrachloride on reaction with molten magnesium yields zirconium metal and magnesium chloride slag (Kroll 1956). The metal and slag could be separated from each other by vacuum distillation.

The Kroll reactor employs a specially designed stainless steel retort and a three zone furnace system for carrying out the reduction reaction. Zirconium tetrachloride and clean magnesium pigs are loaded in separate containers in the retort. After *in situ* purification of the chlorides by pumping out the volatile impurities at 300°C, magnesium is heated to above its melting point (to 850°C), and the chloride is distilled in a controlled manner to react at the surface of molten magnesium. At the end of reduction, remaining excess magnesium and magnesium chloride are separated from the zirconium sponge by pyrovacuum distillation in another heavy walled retort capable of evacuation down to 0.1 Pa at 900°C. Vapour pressures of magnesium and magnesium chloride at 900°C are 13 and 1 kPa, respectively (Kroll 1956; Subramanyam & Sundaram 1966).

Apart from the Kroll process, for the conversion of a zirconium halide intermediate to zirconium metal, a molten-salt electrolysis method has also been considered. The molten salt electrolytic process is an attractive alternative for the continuous production of zirconium. This process, coupled with the fractional crystallization process for the hafnium removal stage, has been successfully commercialized in Russia using pure K_2ZrF_6 as cell feed material. The electrolysis is carried out under argon atmosphere in a graphite lined cell using a fused salt mixture of 20–30% K_2ZrF_6 and 70–80% NaCl or KCl at a temperature of 850°C. The cathode is made of stainless steel, where zirconium gets deposited and the anode is made of graphite where chlorine gas is evolved.

The Van Arkel and de Boer Iodide process is used for further refining of zirconium to produce extremely high purity metal in the form of crystal bar. The process is based on the reversibility of the reaction between the metal and iodine.

$$Zr\,(s) + 2\,I_2\,(g) = ZrI_4\,(g)\,. \tag{1}$$

The forward reaction takes place at a lower temperature of around 200°C in the zone of the reactor where the impure metal is packed, while the reverse reaction takes place at a higher temperature of 1300°C, usually on a self resistance heated filament on to which the pure metal deposits due to thermal decomposition of ZrI_4 (Paul *et al* 1973). The process is carried out in an evacuated vessel along the axis of which a starting filament of the same metal but of high purity is aligned and electrically heated to above the decomposition temperature of the metal iodide, to initiate and sustain the crystal bar growth. The crude metal to be purified is stacked inside the vessel in the annular space between the vessel wall and a concentric screen. Electron beam melting, the details of which have remained proprietary, has also been used on a commercial scale to refine zirconium metal.

3.2 *Development of zirconium alloys*

Dilute zirconium alloys, with minor alloying additions, meet most of the considerations made in selection of nuclear structural materials (Dietz 1994; Lemaignan & Motta 1994; Banerjee *et al* 2002; Williams 1970; Ibrahim & Cheadle 1985; Coleman *et al* 1996; Krishnan & Asundi 1981; Cox 1990; Karlsen & Vitanza 1994; Harding 1993; Bai *et al* 1991; Moulin *et al* 1984). Zirconium alloys like zircaloys (Williams 1970; Ibrahim & Cheadle 1985; Coleman *et al* 1996; Krishnan & Asundi 1981), Zr–Nb alloy (Lemaignan & Motta 1994; Williams 1970; Ibrahim & Cheadle 1985; Coleman *et al* 1996), Zr-1.2Cr alloy, Ozhennite-0.5 (Williams 1970), Zirlo (Moulin *et al* 1984) and Excel (Ibrahim & Cheadle 1985) are being used or developed for use in aqueous, organic and gaseous environment. Zirconium alloys, which have been extensively used in water cooled reactors are zircaloys and Zr-1–2.5 wt.% Nb alloys. The zircaloys (Krishnan & Asundi 1981; Cox 1990; Karlsen & Vitanza 1994; Harding 1993; Bai *et al* 1991; Moulin *et al* 1984), a series of alloy with tin as primary alloying additions, are widely used as cladding material in both pressurized water and boiling water reactors, and as cladding material, pressure tube and calandria tube material in PHWRs (Dietz 1994; Lemaignan & Motta 1994). Typical compositions of zircaloys are given in table 2 (Krishnan & Asundi 1981). Addition of tin provides substantial improvement in corrosion resistance over pure zirconium without seriously affecting the neutron economy (Lemaignan & Motta 1994; Cox 1990; Karlsen & Vitanza 1994; Harding 1993). Zircaloy-1 was developed with 2.5 wt.% Sn, but it showed a transition time above which corrosion rate was found to increase (Dietz 1994; Lemaignan & Motta 1994). Addition of iron, chromium and nickel showed improvement in corrosion property, which led to the development of zircaloy-2 (Zr-1.5 wt.% Sn-0.12 wt.% Fe-0.1 wt.% Cr-0.05 wt.% Ni) (Dietz 1994; Lemaignan & Motta 1994; Krishnan & Asundi 1981). As compared to Zircaloy-1, Zircaloy-2 was found to have better corrosion property at reactor operating temperature of 300°C and almost identical mechanical properties. However, breakaway corrosion associated with Zircaloy-2, due to the presence of Tin, was still a matter of concern (Dietz 1994; Lemaignan & Motta 1994).

Table 2. Chemical compositions of Zircaloys (Krishnan & Asundi 1981).

	Weight % of alloying elements				
Alloy	Sn	Fe	Cr	Ni	Zr and impurities
Zircaloy-1	2.5	-	-	-	Balance
Zircaloy-2	1.5	0.12	0.1	0.05	Balance
Zircaloy-3	0.25	0.25	-	-	Balance
Zircaloy-4	1.5	0.22	0.1	-	Balance

This problem was overcome by developing Zircoloy-3 with the level of Tin restricted to be just sufficient for countering the deleterious effect of nitrogen on corrosion resistance. Tin prevents the generation of vacancies due to nitrogen diffusion by forming a complex with the latter. Analysis of hydrogen pick-up in Zircaloy-2 suggested a detrimental role of Nickel. This led to the development of Zircaloy-4 in which case Nickel was replaced by Iron (Dietz 1994; Lemaignan & Motta 1994). Zircaloys are used as cladding tube, calandria tube and guide tubes in water cooled reactor.

Corrosion resistance has perhaps been more important than mechanical properties in the development of Zircaloys (Dietz 1994; Lemaignan & Motta 1994; Cox 1990; Karlsen & Vitanza 1994; Harding 1993) for pressure tube application. However, the search continued for a high strength dilute zirconium alloys, which could permit the use of thinner components, thereby reducing the loss of neutrons by parasitic absorption in core structural components (Dietz 1994). Russian work strongly suggested that the alloys containing 1–5 wt.% Niobium would have superior mechanical strength and adequate corrosion resistance (Ambartsumyan *et al* 1958). In fact, Zr 2.5 wt.% Nb and Zr 1.0 wt.% Nb alloys were found to be attractive because of their high strengths at the reactor operating temperatures, an improvement in corrosion resistance and consequent reduction in hydrogen pick-up rate. Zirconium 2.5 wt.% Nb alloy is mainly used as the pressure tube material in pressurized heavy water reactor (PHWR), CANDU (Canadian Deuterium Uranium) reactor and RBMK (Russian) reactor (Dietz 1994; Williams 1970; Ibrahim & Cheadle 1985; Fleck *et al* 1993) while Zr 1 wt% Nb alloy is used as cladding tubes in RBMK, VVER and submarine reactors. Though the corrosion resistance of cold worked and stress relieved Zr 2.5Nb alloy used in PHWRs and CANDU reactors is comparable to that of Zircaloys, only a small fraction of nascent hydrogen isotopes generated during corrosion is picked by the Zr 2.5 wt% Nb alloy (Puls *et al* 2004) as the presence of Nb promotes recombination of nascent hydrogen isotope to molecular form, which escapes in the coolant. This resulted in reduced rate of degradation of mechanical properties due lower hydrogen isotope pick up and hence longer life to components made from these alloys.

3.3 *Zirconium alloy components*

The service demands from zirconium alloys for different components in a nuclear reactor are considerably different (Singh *et al* 2007). The respective service demands on these alloys for different components in a reactor are in fact met with by judicious use of anisotropic deformation behaviour of hexagonal close packed (hcp) crystal structure of zirconium. The anisotropic deformation behaviour of zirconium is apparent from differences in the ratios of transverse to longitudinal and transverse to biaxial strength. This anisotropy in strength values is the result of a strong crystallographic texture formation, which is dependent on the degree of deformation, thermo-mechanical history and composition of the alloy. Although the pressure tubes are fabricated following similar routes the texture developed in Zircaloy-2 appears to be more beneficial to biaxial ductility and to biaxial strength than that generated in Zr-2.5 wt.% Nb alloy (Singh *et al* 2007). The hydrogen picked up during service in reactors leads to the formation of hydrides in zirconium alloys (Singh 2002; Northwood & Kosasih 1983). The zirconium hydrides precipitated have deleterious effect on the mechanical properties. The hydrides form along a specific habit plane $(10\bar{1}7)$, which is close to the basal plane (Westlake 1968). The deleterious effect of hydrides is reduced by controlling the texture so as to precipitate the hydrides in direction, which is parallel to the hoop stress (Singh *et al* 2007; Singh 2002; Northwood & Kosasih 1983). Excessive irradiation creep and growth are the other two important life limiting factors in the

zirconium alloys in reactors. The adverse effects of these two factors are controlled by an optimum level of cold work and appropriate choice of the annealing temperature (Singh *et al* 2007).

3.3a *Cladding tubes*: Thin tubes made of either zircaloys or Zr-1.0 wt.% Nb alloy are used to encapsulate fuel pellets in order to prevent its contact with coolant in water cooled reactors. Fuel cladding can be grouped into two classes, namely, collapsible and free standing. While the former finds application in PHWRs, the latter is used in Pressurized Water Reactors (PWRs) and Boling Water Reactors (BWRs). During reactor operation, UO_2 pellets (encapsulated in cladding tubes) expands more than Zircaloy cladding, is hotter, cracks and swells resulting in straining of the cladding under multiaxial stress that could cause localized wall thinning. Zircaloy clad is subjected to aqueous corrosion during service resulting in release of nascent hydrogen. A part of nascent hydrogen isotopes thus evolved is picked by the clad tube and makes later susceptible to hydride embrittlement. The pellet clad interaction and hydride embrittlement are the primary life limiting factor for the cladding tubes. Thus, in addition to specifying mechanical properties such as tensile properties, creep rate, fatigue endurance (high cycle and low cycle fatigue), the satisfactory performance of cladding tube in an operating fuel element are achieved by ensuring hydride orientation, which is least deleterious and is resistant to stress reorientation. This is ensured by having more than 80% of basal poles oriented along radial direction of the Zircaloy clad tubes. The mechanical properties degrade during service due to increase in hydrogen content, temperature and by neutron irradiation. The most important limiting aspect of mechanical performance, however, has been recognized as tensile ductility under multi-axial stress condition (Singh *et al* 2007). Therefore, the ductility of fuel cladding is specified as ∼15% to give allowance for the permissible reduction up to 2% during irradiation to ensure integrity during service. Transverse strength and total circumferential elongation (TCE) are of prime importance for free standing cladding tubes used in PWRs and BWRs. The stringent requirements of high strength and high TCE of these tubes can be met by introducing a heavy reduction in wall thickness in the final stages of pilgering followed by annealing at an optimum temperature where the material is just recrystallized to produce a fine grained structure free of residual stress. This fabrication schedule also generates a radial basal pole texture >80%, which would assure hydride plates along the circumferential direction, high transverse strength and greater resistance to localized wall thinning.

3.3b *Pressure tubes*: Pressure tubes also called coolant tubes are the heart of PHWRs. The hot pressurized heavy water coolant, fuel bundle weight and irradiation produce an environment of temperature, stress, corrosion, and radiation damage. Such an environment leads to changes in dimensions (creep and growth); in mechanical properties (increase in strength and DHC velocity, decrease in ductility and fracture toughness); in microstructure (globurisation of β-phase particularly in Zr-2.5 Nb alloy, change in dislocation density) and chemical composition (particularly hydrogen content and Nb content in β-Zr phase). 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. This is achieved by assuring that the pressure tubes during service in the reactor retain a minimum level of fracture toughness. Thus the requirements for pressure tube alloys differ from those for fuel cladding, largely because of the facts 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 (Singh *et al* 2007).

In early generation PHWRs Cold-worked Zircaloy-2 tubes were used as pressure tubes with design life of ~15 years. The design of the pressure tube is based on section III of the ASME pressure vessel code, which specifies the criteria of maximum design stress on the basis of ultimate tensile strength, yield strength, creep and stress-rupture strengths at the operating temperature (Singh *et al* 2000). For pressure tube alloys (both Zircaloy-2 and Zr-2.5 Nb alloy) one third of the ultimate tensile strength has been found to be the limiting property. Since Kakrapara-2 onwards pressure tubes made of Zr-2.5 Nb alloy are being used to achieve better in-reactor performance. All the earlier generation Indian PHWRs used Zircaloy-2 as pressure tubes. Although pressure tubes of this material served satisfactorily in reactor applications, it is now known that Zircaloy-2 suffers from high rates of hydrogen pick up and somewhat high rates of irradiation induced creep. Though internationally Zr-2.5 Nb alloy has been tried in two different conditions: conventional cold worked and stress relieved and heat treated (quenched and aged) state (Coleman *et al* 2007), in India and Canada due to ease of fabrication and economic reasons Zr-2.5 Nb alloy is used as pressure tube in cold worked and stress relieved condition. The heat-treatment for the quenched and aged condition is carried out almost at the last stage after which very little cold work is imparted.

3.3c *Calandria tubes*:   In PHWRs hot pressure tube is surrounded by a concentric tube called calandria tube that is at ~70°C and is surrounded by heavy water moderator which is not pressurized. They experience neither a high stress value nor high temperatures during service but they are expected to serve the entire design life of these reactors. The current fabrication practice of calandria tubes includes steps such as sheet rolling followed by tube forming, seam welding, rolling to level the welded seam and vacuum annealing. Recently adopted practice has also produced calandria tubes which avoids welded seam. The fabrication steps are so designed that the irradiation growth of these tubes remains within a tolerable limit during the design life of a PHWR (Singh *et al* 2007).

Besides these important alloys, Zr-2.5 Nb-0.5Cu alloy is used for making garter springs which are located in the annulus gap between the pressure tube and calandria tube and thereby separate hot pressure tubes coming in contact with the cooler calandria tubes. The garter spring should have adequate strength and ductility and should retain sufficient crushing strength during their service life. In PHWRs a coolant channel comprises of fuel bundles, a pressure tube, garter springs and a calandria tube. Several coolant channels are mounted horizontally in a vessel of SS304L called calandria vessel.

3.4 *In-service degradation*

It is evident from the above discussion that the property requirements for various components like fuel cladding tubes, pressure tubes, calandria tubes and garter spring, are quite diverse (Singh *et al* 2007). It is only through the proper control of processing parameters that, such a diverse specification are met using the same zirconium alloy. In addition to the mechanical properties, the specifications include crystallographic texture, grain size and shape, degree of cold work and dislocation density, which in fact help to achieve the desired properties (Singh *et al* 2007). Two main life limiting factors associated with fuel tubes were hydride embrittlement and iodine-induced stress corrosion cracking (SCC), as a result, of pellet-clad interaction. By producing fuel

tubes with the basal poles predominantly along the radial direction of the tubes, hydride embrittlement problem is greatly reduced. Similarly, by imparting a thin layer of graphite on the inside diameter of the fuel tube the SCC problem due to iodine is significantly reduced for the fuel tubes meant for use in PHWRs. Calandria tube is exposed to low temperature and low stress and hence excessive deformation and creep is not of much significance. But irradiation growth does pose some concern. Garter spring possesses high 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 and so far no failure have been reported (Singh *et al* 2007). The major concern for Garter spring is their displacement from their designed location, which is also greatly reduced by employing tight fit springs. Moreover, these components are not the final pressure boundary containment structures. The major challenge for PHWR safety from metallurgical perspective is posed by the pressure tubes (Singh *et al* 2007), being the component in the pressure boundary. The main in-service degradation mechanisms are hydride embrittlement, irradiation embrittlement and in-reactor dimensional changes.

3.4a *Hydride embrittlement*:   Hydrogen damage has been identified as a primary life limiting factor for pressure tubes and secondary life limiting factor for clad tubes (Singh 2002; Northwood & Kosasih 1983). The operating condition for other zirconium alloy components is such that hydrogen damage is not a concern for their safe operation. The maximum allowable hydrogen content in the both fuel tube and pressure tubes was limited to 25 ppm by weight. Later on for pressure tubes specified limit for hydrogen content in the as manufactured condition was reduced to 5 wppm, which was achieved by adoption of quadruple melting and machining the surface layers during fabrication. During service part of the hydrogen/deuterium evolved from coolant-metal corrosion reaction is picked up by these components. Hydrogen present in excess of solid solubility (Singh *et al* 2005) precipitates out as hydride phase, which is known to embrittle the host matrix (Singh 2002; Northwood & Kosasih 1983).

The maximum amount of hydrogen which can be retained in solid solution without forming hydride precipitate is called Terminal Solid Solubility (TSS) (Singh *et al* 2005). TSS of hydrogen in these alloys is an important parameter and is used by design and safety engineers for fitness for service assessment of these components. Experimentally TSS (Northwood & Kosasih 1983) is determined by preparing samples with known concentration of hydrogen and measuring some change in physical property to identify transition temperature. Techniques like dilatometry, resistivity, internal friction, differential scanning calorimetry, small angle neutron scattering and metallography measure changes in dimension, resistance, damping frequency, heat flow, lattice parameter and microstructural features, respectively, and are used to determine the transition temperature. The experimentally determined transition temperature is correlated with hydrogen concentration in the form of an Arrhenius type relationship to obtain the pre-exponential constant and the enthalpy of the dissolution (heating) or precipitation (cooling) process. With the help of these constants TSS at any temperature can be obtained. Also, for a sample of unknown hydrogen concentration by determining the transition temperature corresponding to heating and/or cooling total hydrogen content of the sample can be estimated non-destructively using the aforementioned constant. Hydrogen content of an unknown sample can also be determined by direct methods like inert gas fusion (IGF) and hot vacuum extraction. It is important to mention here that the TSS of hydrogen in zirconium alloys is not significantly affected by minor alloying additions typical of zirconium alloy chemistry used in water cooled nuclear reactors but exhibit strong temperature dependence due to hysteresis. TSS obtained during cooling (TSSP) is almost twice that obtained during heating (TSSD) in the temperature range between ambient and reactor

operating temperature of ∼300 C. Figure 1 shows the variation in TSSP and TSSD for zirconium alloys.

Hydrogen in excess of solid solubility precipitates as hydride phase. Depending on the hydrogen concentration and cooling rate employed one meta-stable hydride (γ-hydride) and two stable hydrides (δ- and ε-hydride) can form in zirconium alloys (Banerjee & Mukhopadhyay 2007). Both fuel tube and pressure tube material comprise primarily of α-Zr phase having close packed hexagonal crystal structure and for the cooling rate possible during operation δ-hydride form in these components. Because of the strain energy associated with the accommodation of δ-hydrides in α-Zr phase, the former acquires plate shaped morphology. The orientation relationship between the δ-hydrides and α-Zr phase is such that the broad face of δ-hydrides is oriented parallel to the basal plane of α-Zr phase. Hydride plates oriented normal to tensile stress are considered most deleterious as it provides easy crack propagation path (Northwood & Kosasih 1983). The hydrogen damage in fuel tubes is minimized by imparting a texture with greater than 80 percent of basal poles in radial direction of the cladding tube. Thus susceptibility to gross hydride embrittlement of cladding tubes is controlled by exercising texture control. A typical micrograph showing traces of hydrides (dark lines) in zircaloy clad on radial-circumferential plane is shown in figure 2. As is evident from this mircograph the traces of hydrides are oriented preferentially along circumferential direction of cladding tube. In fact, measurement of radial hydride fraction (F_N number) in the hydrogen charged cladding tubes is routinely used as a quality check to assess the susceptibility of cladding tubes to hydride embrittlement (IAEA-TECDOC-1649 2010).

A typical micrograph revealing hydrides in Zr-2.5 Nb pressure tube material is shown in figure 3a. For given hydrogen content two features of the traces of hydride on radial-circumferential (RC) plane and that on the axial-radial (AR) plane of the pressure tube are to be noted in this figure (Singh *et al* 2006). Firstly, the trace on radial-axial plane is straighter and longer as compared to the trace on radial-circumferential plane. It may be noted here that the texture of the pressure tube is such that crystallographically both radial and circumferential hydrides can form. However, due to preferentially aligned grain-boundaries only circumferential hydrides form in pressure tube material. This is called microstructure control of hydride orientation.
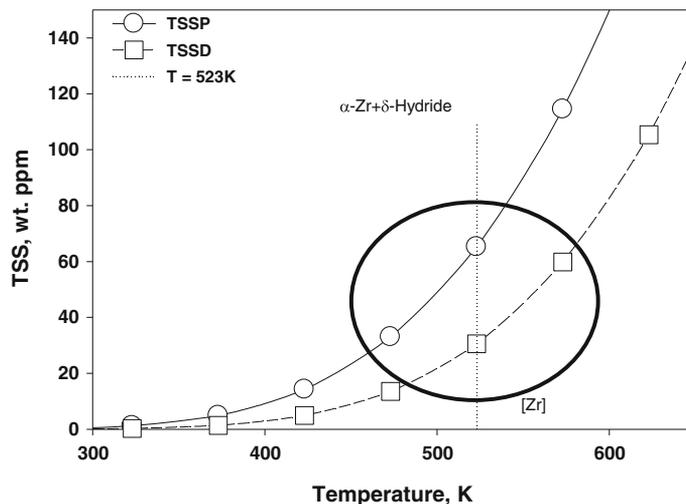

Figure 1. Typical variation in TSSP and TSSD for dilute zirconium alloys as a function of temperature.
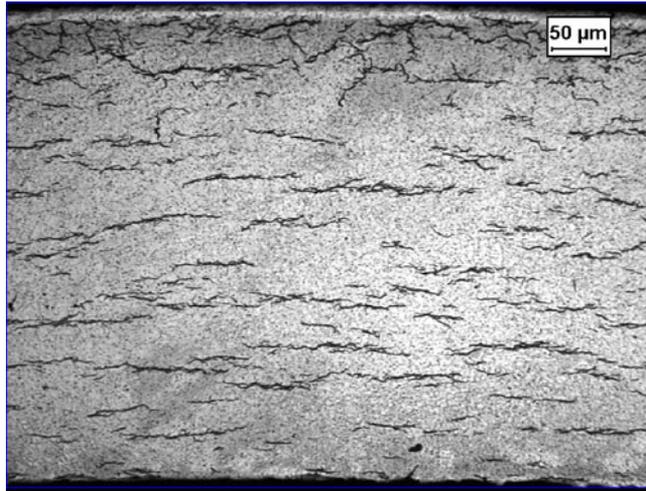
Figure 2. Optical micrograph of zircaloy-2 cladding material containing 270 ppm of hydrogen. Dark lines are traces of circumferential hydrides. As is evident from this micrograph traces of hydrides oriented along radial direction are negligible (IAEA-TECDOC-1649 2010).

Interesting microscopic details of the circumferential hydride plates are brought out in figure 3b. The hydride plates, which appear as a single entity under an optical microscope, show two sub-microscopic levels of organization. At platelet level of organization, the hydride plates comprise of several smaller hydride platelets stacked with a near parallel orientation with respect to each other. At sub-platelet level of organization each hydride platelet was observed to be comprising of several tiny sub-platelets stacked closely either laterally or end to end (Singh *et al* 2006).

Hydrides being brittle make the host matrix susceptible to embrittlement. Two forms of hydride embrittlement have been recognized for hydride forming metals—gross and localized (Singh 2002). The former requires certain minimum volume fraction of the hydride phase and results in overall reduction in tensile ductility, impact and fracture toughness. Since hydride
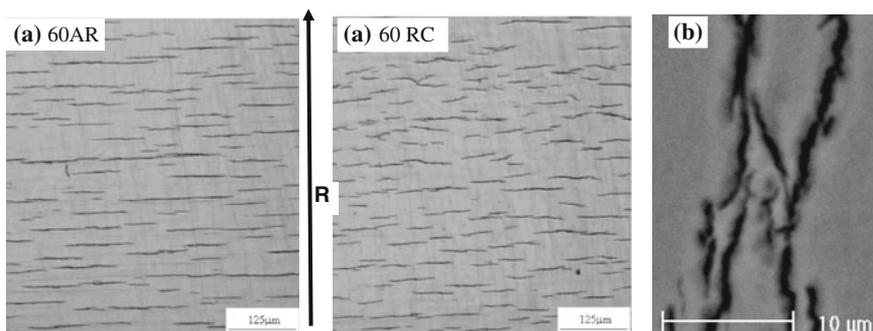

Figure 3. (**a**) The microstructural features of traces of hydrides on AR and RC planes of Zr-2.5 Nb pressure tube alloy charged with 60 ppm of hydrogen. Arrow shows the radial direction and axial or circumferential direction in these micrographs is normal to it (Singh *et al* 2006). (**b**) Internal details of circumferential hydride as observed in secondary electron mode (Singh *et al* 2006).

embrittlement is a major life limiting factor for the components made from these alloys, several theoretical and experimental studies have been carried out to understand the influence of hydrogen/hydride on the mechanical properties in general and micromechanisms assisting crack nucleation and its propagation in the presence of hydride, in particular (Singh *et al* 2013). The pressure tube is a pressure boundary component and its design is based on the leak before break (LBB) concept, which requires that any crack/flaw in this component should leak already at a length that is less than critical crack length for catastrophic failure of these components. During fabrication of cold worked and stress-relieved (CWSR) Zr-2.5 Nb pressure tube, a majority of the α-Zr grains acquire an orientation with their basal poles oriented predominantly along the circumferential ($\sim$55%) and radial ($\sim$43%) direction (Srivastava *et al* 1995). Since hydride precipitation in α-Zr grains show a habit plane nearly parallel to basal plane (Westlake 1968), for the texture of the pressure tube material, crystallographically only two orientations are permissible. These are along the circumferential-axial plane and along the radial-axial plane. Hydride platelets oriented along the circumferential-axial plane are called circumferential hydrides and those oriented along radial-axial plane are called radial hydrides (Northwood & Kosasih 1983). Under unstressed condition, only circumferential hydrides form in Zr-2.5 Nb pressure tubes. The influence of hydrogen content and temperature on the axial fracture toughness parameters of unirradiated double melted Zr-2.5 Nb pressure tube alloys is shown in figure 4 (Singh *et al* 2013). Singh *et al* (2013) reported that the fracture toughness parameters representing crack initiation, such as J_Q, $J_{0.15}$ and K_{JC} were practically unaffected by hydrogen content and temperature (figure 4a). The fracture toughness parameters representing crack propagation, such as J_{max}, $J_{1.5}$, K_{max} and mean dJ/da (figures 4a and b) were practically unaffected by hydrogen content but showed strong temperature dependence. The crack propagation fracture toughness parameters increased with temperature to a saturation value. The fracture toughness parameters can be used to assess the susceptibility of pressure tubes to fracture. An understanding of micromechanisms of fracture led to adoption of quadruple melting practice and use of selected raw materials to produce Zr-2.5 Nb pressure tubes having lower impurity content resulting in enhanced initial toughness. The most important fracture toughness parameter is critical crack length, which is used of checking adherence to LBB criteria. It is determined by burst test or from J_{max} values obtained using small compact tension samples. Though the values of CCL obtained using small
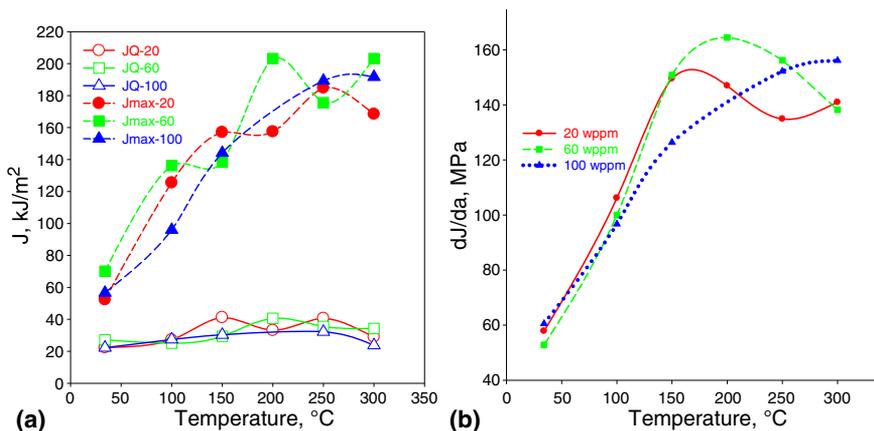

Figure 4. Temperature dependence of (**a**) J_Q and J_{max} (kN/m), (**b**) dJ/da of CWSR Zr-2.5 Nb pressure tube (N/m^2) with a hydrogen content of 20, 60 and 100 wppm (Singh *et al* 2013).

samples are conservative, it is extensively used method. The variation in critical crack length for the catastrophic failure of pressure tubes under reactor operating condition with hydrogen content and test temperature is shown in figure 5 (Singh *et al* 2013). The value of CCL computed from J_{max} values by iterative method in the present investigation was >44 mm for all the hydrogen concentrations and test temperatures. The CCL value was greater than 55 mm for tests carries out at temperatures greater than 150°C. Since J_{max} values were not affected by hydrogen content, CCL too was insensitive to hydrogen content.

The pressure tube design is based on the concept of leak before break (LBB). Since the pressure tube thickness is about 4 mm, for a circular crack the CCL should be greater than 4 mm for LBB criteria to be satisfied. Usually the cracks observed in pressure tubes are of elliptical shape of aspect ratio between 4 and 7 with major dimension oriented along the axial direction of tube. Thus for LBB criteria to be satisfied CCL of the operating tubes should be greater than 7 times the wall thickness i.e., ~28 mm. The CCL value reported in this work is component-specific and for unirradiated material. With irradiation the CCL values decrease. The CCL values of the as-manufactured pressure tube material should be sufficiently greater than 28 mm to leave sufficient margin for safe operation of these components.

As described earlier, circumferential hydrides do not seem to affect the fracture toughness parameters significantly. However, due to stress reorientation phenomenon, radial hydrides may precipitate and being oriented normal to hoop stress direction of the pressure tubes, can significantly increase the latter's susceptibility to failure (Singh *et al* 2004a). The phenomenon of precipitation of radial hydrides, when cooled under stress from solution annealing temperature is known as stress-reorientation of hydrides. For dilute zirconium alloy pressure tubes this translates to precipitation of radial hydrides under hoop stress as compared to the precipitation of circumferential hydrides in the unstressed condition. This is usually associated with a critical stress called threshold stress below which no reorientation occurs.

The threshold stress for reorientation of hydrides was determined using a hydrogen charged tapered gage tensile specimen, heating it to a solution annealing temperature to dissolve all the hydrides, cooling from solution annealing to a reorientation temperature, applying a constant
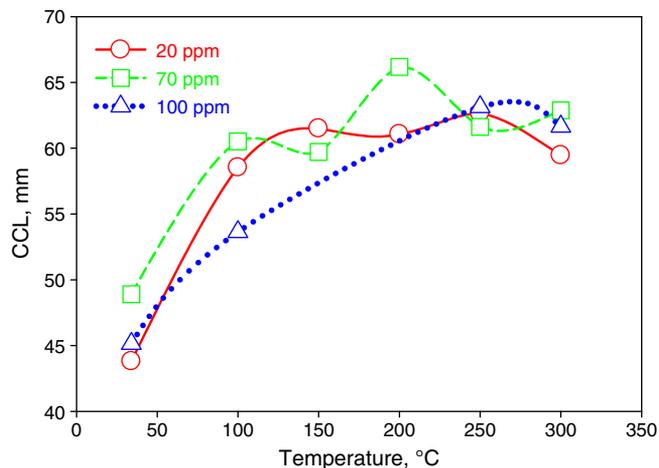

Figure 5. CCL (mm) for catastrophic failure of Zr-2.5 Nb pressure tubes under PHWR operating condition computed from J_{max} values at various test temperatures and hydrogen contents (Singh *et al* 2013).

load so as to attain stress variation across the specimen axis, and allowing the specimen to cool under fixed load. After cooling, the specimen is slit axially, examined metallographically for hydride orientation, a montage is prepared for the entire sample, the boundary between radial and circumferential hydride is marked and local and mean threshold stresses are determined (Singh *et al* 2004a). The threshold stress for reorientation of hydrides in CWSR Zr-2.5 Nb pressure tube material is shown in figure 6 (Singh *et al* 2004a) and is observed to decrease with increase in reorientation temperature. For cold worked and stress relieved pressure tube material the threshold stress for reorientation of hydrides is in the range of 60–80 percent of the yield strength but is expected to depend on the basal pole fraction oriented along circumferential direction. During service designers have to ensure that the sum of hoop stress and the residual stress in the operating pressure tubes is less than the threshold stress for reorientation of hydrides to prevent formation of radial hydrides. It is worth mentioning here that the threshold stress reorientation of hydrides for Zircaloy-2 pressure tubes was 90–120 MPa which was comparable to hoop stress of the order of 110 MPa. The threshold stress for Zr-2.5 Nb alloy pressure tubes are >200 MPa which higher than the hoop stress of 135 MPa.

Figure 7 shows the variation in percent elongation and reduction in area as a function of test temperature for Zr-2.5 Nb pressure tube material containing 100 wppm of hydrogen. These samples were subjected to stress reorientation treatment and had predominantly radial hydrides. At room temperature, both percent elongation (plastic) and reduction in area were 0, indicating the strong embrittling influence of reoriented/radial hydrides. With the increase in test temperature, the tensile elongation to failure and reduction in area were found to increase (Singh *et al* 2004a).

Delayed Hydride Cracking (DHC) (Singh *et al* 2002, 2004b, 2009a; Chow *et al* 1991) is a form of localized hydride-embrittlement phenomenon, which in the presence of a hydrostatic stress-field manifests itself as a sub-critical crack growth process. It is caused due to hydrogen migration up the hydrostatic stress gradient to the region of stress concentration. Once the local solid solubility is exceeded, brittle hydride nucleates normal to tensile stress. Growth of hydride nuclei continues till hydride platelet of a critical size is formed. Hydride platelet of the critical size cracks under concentrated stress leading to the growth of the crack. This crack growth is
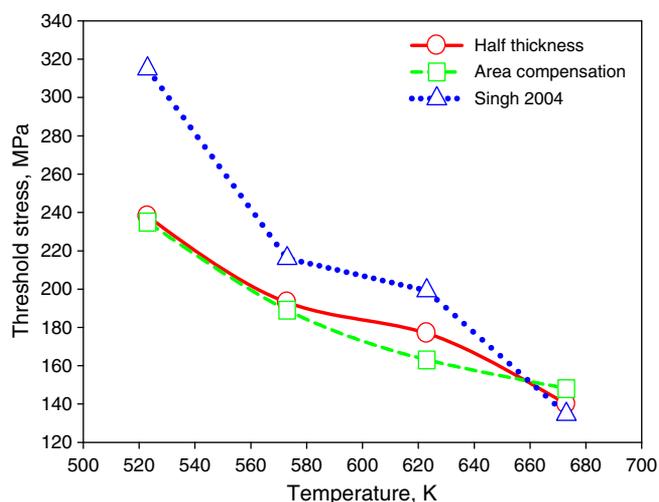

Figure 6. Variation in mean threshold stress (MPa) with reorientation temperature (Singh *et al* 2004a) for Zr-2.5 Nb pressure tube material.
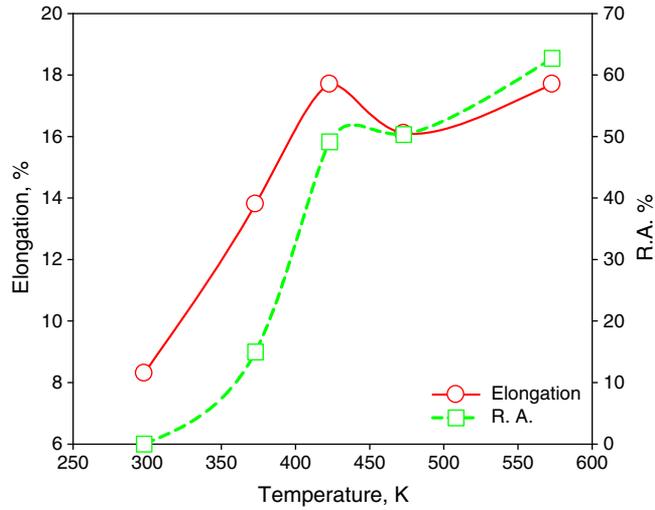
Figure 7. Variation in total elongation and reduction in area (R.A.) with test temperature for Zr-2.5 Nb pressure tube material containing 100 ppm hydrogen and subjected to reorientation treatment (Singh *et al* 2004a).

delayed by the time required for hydrogen to reach the crack tip and form hydride platelet(s) of critical size. Hence this phenomenon is called Delayed Hydride Cracking.

DHC is a discontinuous crack growth process and is usually associated with an incubation period to crack initiation, a stable crack growth velocity called DHC velocity (V_{DHC}) and a threshold stress intensity factor - SIF (K_{IH}) (Singh *et al* 2009a). Below K_{IH}, V_{DHC} is negligible, and above this threshold V_{DHC} increases rapidly with increase in SIF up to K_{IY} (SIF corresponding to initiation of plastic yielding at the crack tip). For SIF greater than K_{IY}, V_{DHC} is independent of the SIF. A second higher threshold SIF corresponds to fracture toughness of the material above which crack grows in an unstable manner. V_{DHC} is influenced to a varying degree by test temperature, direction of approach of test temperature, strength of alloy, hydrogen content, crystallographic texture, and microstructure of the material. Both V_{DHC} and K_{IH} are important for designer for safety assessment. An estimate of V_{DHC} is required in ascertaining the applicability of LBB criteria for pressure tube as per eq. (2).

$$t < ((CCL - a_{\text{leak}})/2V_{DHC}), \tag{2}$$

where t is operator's response time, *CCL* is critical crack length, a_{leak} is the crack length at leak detection and factor 2 in the denominator is to consider two-sided crack growth by DHC. Similarly, K_{IH} is used to estimate the flaw size which can be tolerated in the component without any increase in flaw size due to DHC. The variation in maximum hydrostatic stress ahead of a sharp crack computed using ABAQUS FEM package is shown in figure 8 as a function of stress-intensity factor for Zr-2.5 Nb alloy having different yield strengths (Singh *et al* 2009a). Initially maximum hydrostatic stress increases almost linearly with increase in stress intensity factor and attains a saturation value. After attaining the saturation value the maximum hydrostatic stress is independent of stress intensity factor similar to the dependence of DHC velocity on stress intensity factor.
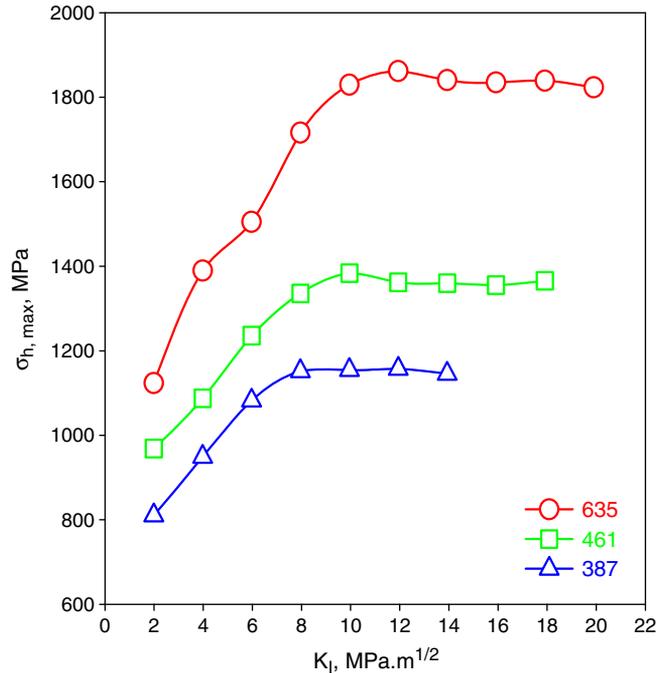
Figure 8. Variation in maximum hydrostatic stress with stress intensity factor for Zr-2.5 Nb alloy having different yield strength (Singh *et al*, unpublished work).

Figure 9 shows the plot of DHC velocity with inverse of the test temperature for CANDU, RBMK and Indian pressure tube material (Singh *et al* 2004b). The temperature dependence of V_{DHC} obtained by linear regression analysis is also shown in this figure. The superscripts denote the source of the material. At a given test temperature, the DHC velocity for the Indian and the CANDU pressure tubes, both of which are used in cold worked and stress-relieved (CWSR) condition, are comparable whereas the DHC velocity in RBMK pressure tube, which is used in quenched and aged condition, is about 2 to 3 times lower than that in CWSR pressure tubes. The variation in DHC velocity (V_{DHC}) with stress intensity factor (K_I) is shown for Indian pressure tube material in figure 10 as a function of test temperatures. For a stress intensity factor (K_I) >15 MPa.m$^{1/2}$, DHC velocity is practically independent of the SIF and below this value DHC velocity decreases appreciably with decrease in K_I. The extrapolation of the plots suggests a threshold stress intensity (K_{IH}) value for DHC in unirradiated double melted cold worked and stress relieved Zr-2.5 Nb pressure tube alloy is about 9–11 MPa.m$^{1/2}$ for the temperature range of 203–283°C (Singh *et al* 2009a).

Figure 11 compares temperature dependence of DHC velocities in Zircaloy-2 cladding material under different microstructural condition (IAEA-TECDOC-1649 2010). It can be seen from this figure that above a critical temperature (283°C) DHC velocity shows either a significant decrease or is negligibly small for some microstructural conditions.

In PHWRs, Calandria tube (CT) surrounds the PT concentrically from outside and separates the cool moderator (at ~80°C) from hot coolant (at 250–293°C). Though, Garter springs are provided at regular intervals in the annulus gap between the PT and CT to prevent PT–CT contact, either due to garter spring displacement from the designed location or due to creep or both,
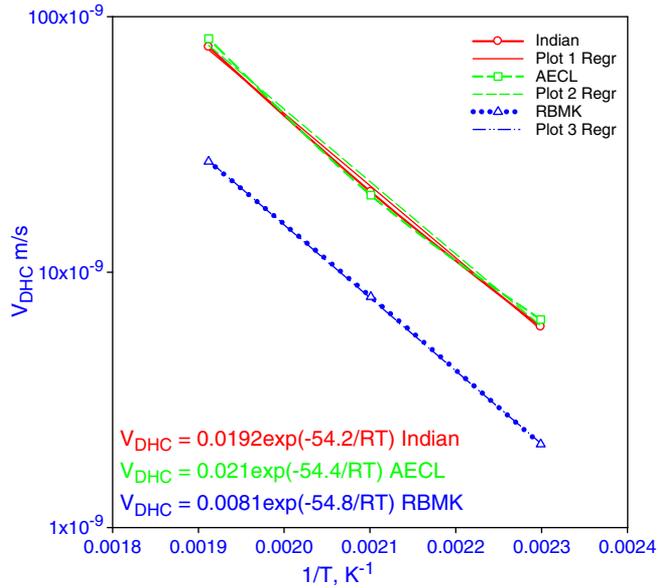
Figure 9. Plot of DHC velocity (V_{DHC}) in Zr-2.5 Nb pressure tube materials with inverse of test temperature (Singh *et al* 2004b).
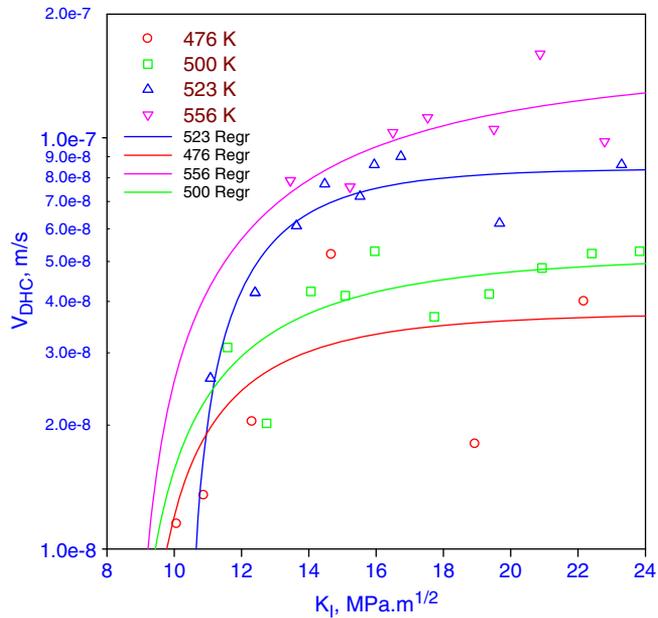

Figure 10. Plot of DHC velocity with stress intensity factor for unirradiated cold worked and stress-relieved Zr-2.5 Nb Indian pressure tube samples tested at various temperatures (Singh *et al* 2009a).
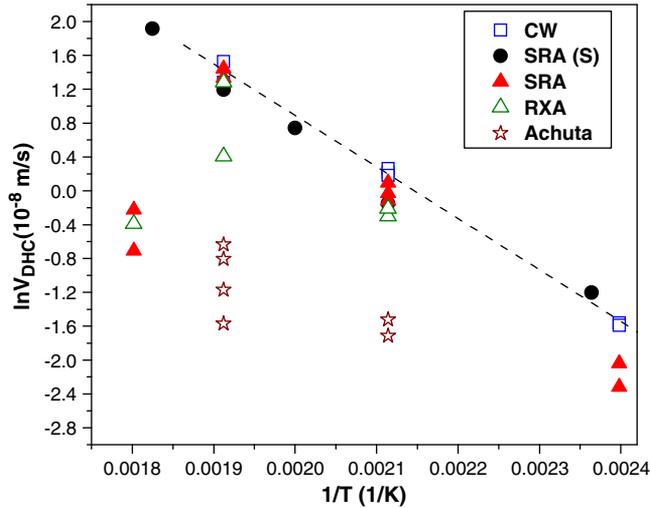
Figure 11. Comparison of variation of DHC velocity with temperature (IAEA-TECDOC-1649 2010).

the PT sags, and may contact CT, resulting in setting-up of thermal gradient in the PT. Hydrogen migration under thermal gradient in zirconium alloys results in formation of hydride blisters. An array of blisters makes zirconium alloy components of nuclear reactors susceptible to fracture. The whole process of hydride blister formation and fracture of these components is very complex and involves hydrogen migration under thermal gradient, hydride precipitation, straining of the matrix, setting up of hydrostatic stress gradient, enhanced hydrogen migration under the combined influence of thermal and stress gradient, stress-reorientation of hydrides, cracking of hydrides, crack growth by delayed hydride cracking mechanism, interlinking of blisters and spontaneous fracture of the component. However, hydride blister formation in zirconium alloys is associated with a critical hydrogen concentration called blister formation threshold (BFT) below which hydride blisters cannot form even in contacting channels. BFT is reported to be ∼30 wppm of hydrogen. With the adoption of quadruple melting practice pressure tube are being produced with hydrogen content less than 5 ppm and at a hydrogen ingress rate of ∼1 ppm/year, hydride blisters are unlikely to form in the operating tubes by the end of design life of 30 years. Also, use of four-number of tight fit garter springs precludes the PT–CT contact.

3.4b *Irradiation effects*: Neutron irradiation is the most important source of radiation damage in zirconium alloys (Banerjee *et al* 2002; Singh *et al* 2007). As a nominal amount of 25 ev of energy is required to displace a Zr atom from its regular lattice position, a single neutron of energy 1 MeV is capable of creating several hundreds of displaced Zr atoms. Many of the displaced atoms would form interstitials and corresponding vacancies in the lattice. These point defects cause the microstructure to change with irradiation. Small vacancy cluster form microvoids, depleted zones and dislocation loops. Interstitials cluster form dislocation loops and formation of defect-cluster-solute atom complexes are also facilitated due to irradiation. Part of the lattice defects produced by irradiation would be annihilated by processes like recombination of interstitials and vacancies. The extent of annihilation of lattice defects would be dependent on temperature. Interstitials and vacancies with higher thermal energy, for example, would have

higher probability for recombination. Thus, the population of lattice defects would reduce at higher irradiation temperatures, and would not be significant if irradiation temperature could be maintained at a suitable higher temperature. However, this temperature happens to be beyond 400°C for zirconium alloys. The zirconium alloy components operate at temperatures in the range 60–300°C, and therefore would undergo irradiation damage. The component materials during their initial period of stay in an operating reactor would keep on accumulating lattice defects. As more and more defects are produced by longer duration of neutron exposure, a stage would come when there would be a dynamic equilibrium between the rate of generation of the defects and their rate of annihilation. Beyond this stage any further increase in total neutron exposure would not lead to further lattice defects and therefore the irradiation-induced changes in the mechanical properties would exhibit a tendency towards saturation.

The irradiation-induced defect clusters described above act as obstacle to dislocation slip thereby increasing the structure sensitive fundamental properties (Yield strength) and to a lesser extent tensile strength. This would result in exhaustion of the capacity for substantial work-hardening once plastic straining begins. This would make the necking to start early in the plastic range. Thus irradiation leads to hardening of the material resulting in reductions in tensile ductility and fracture toughness. Another consequence of increased strength is the increase in DHC velocity and reduction in the threshold stress intensity factor for initiation of DHC from ~ 10 MPa.m$^{1/2}$ to less than 5 MPa.m$^{1/2}$. Mechanical properties are reported to saturate before attaining a total neutron exposure of $\sim 5 \times 10^{25}$ n/m^2 (Chow *et al* 1991). The end of life fluence of Zr-2.5 Nb alloy pressure tubes exceed this value by an order of magnitude and thus would experience significant irradiation damage.

At the operating temperature (~ 300°C) of nuclear reactors thermal creep rate in zirconium alloys is not of serious concern, though, in the presence of radiation the creep rate is considerably enhanced. In fact, recent results indicate that of the two mechanisms (creep and irradiation growth) responsible for dimensional changes, the contribution from creep deformation is much higher than that from the growth process. Thus, it appears that dimensional change caused by irradiation creep can be the life limiting factor for highly stressed components such as pressure tubes. Irradiation enhances the rate at which thermal creep mechanism such as jog dragging, dislocation climb/glide and solute trapping proceeds. All these mechanisms, therefore, can be grouped under radiation enhanced creep. It has been noted that solutes such as tin, iron, chromium, oxygen and nickel significantly affect the irradiation creep and thermal creep strength through their effects on solid solution hardening, stacking fault energy and diffusion rate. Cold working, in general, increases the in-reactor creep rate. Grain size variation within normally used range 10 to 20 μm has marginal effect on creep rate although the grain shape (aspect ratio) influences the irradiation growth (Lemaignan & Motta 1994; Franklin *et al* 1983).

Partitioning of irradiation-induced excess vacancies and interstitials to anisotropically distributed sinks such as dislocations and grain-boundaries would cause preferential growth in <a> direction and contraction in <c> direction, thereby introducing a specific phenomenon called irradiation growth. Irradiation growth is influenced by alloy composition, extent of cold work, residual stress and irradiation variables such as flux and temperature. It has been observed that the growth strain in cold worked material is considerably higher than that in recrystallized material and increases linearly with fluence. It may be noted that, in order to mitigate the influence of the irradiation creep and growth, metallurgical and microstructural factors such as crystallographic texture, total dislocation density, types of dislocations, grain size and shape, and phase content and distribution are to be considered for optimization (Singh *et al* 2007).

3.5 *Mitigation of in-service degradation*

In early generation PHWRs hydride embrittlement was the life limiting factor for pressure tubes. The hydride embrittlement problem was addressed by changing pressure tube material from Zircaloy-2 to Zr-2.5 Nb alloy, adopting quadruple melting practice instead of double melting, improved roll joint and use of four number of tight fit garter springs instead of two garter springs used earlier. However, present concern for the cold worked and stress relieved (CWSR) Zr-2.5 Nb alloy pressure tubes is excessive diametral creep, excessive axial elongation and variability in axial elongation resulting in interference with feeder pipes and other structurals.

A literature survey (Coleman *et al* 2007) of the manufacturing practices of the Zr-2.5 Nb alloy pressure tubes revealed that this alloy is used in four metallurgical conditions, viz., cold worked and annealed (Russia); cold worked and stress-relieved (Canada, India, South Korea); and water quenched and aged (Russia, Japan) and Gas quenched and aged (Russia). The cold worked and annealed tubes and gas quenched and aged tubes have much lower strength and do not meet the short term strength requirement of the pressure tubes for Indian heavy water reactors. Cold worked and stress relieved Zr-2.5 Nb pressure tubes reportedly show low in-reactor dimensional changes at lower fluences and shows accelerated behaviour at larger fluences (Coleman *et al* 2007). On the other hand, heat-treated Zr-2.5 Nb pressure tubes reportedly show linear increase in in-reactor dimensional change with fast neutron fluence and appear to be showing better resistance to in-reactor dimensional changes (figure 15 of Coleman *et al* (2007)). Irradiation growth, thermal creep and irradiation enhanced creep are the main in-reactor deformation modes for Zr-2.5 Nb alloy pressure tubes and are reportedly influenced by intrinsic parameters such as alloy chemistry, grain-size and its aspect ratio, texture, dislocation type and its density and extrinsic parameters such as temperature, operating stress and fluence (Coleman *et al* 2007). Thus a need was felt to revisit the design limits, alloy chemistry and manufacturing practice of Zr-2.5 Nb alloy pressure tubes for existing fleet of PHWRs and new generation reactors such as PHWR700 and AHWRs.

Cold worked and stress-relieved (CWSR) tubes are already being used in IPHWRs and within 15–20 years of operation the design limit of 3% diametral creep will be exhausted. Based on an analysis of the thermal hydraulics and structural integrity of the coolant channels it has been suggested that pressure tubes can be safely operated till 4% of the diametral creep. The alloy chemistry and fabrication parameters have also been critically examined to further enhance the in-reactor performance of the CWSR tubes. It has been decided to enhance the oxygen and iron content, and reduce the carbon content because of their effect on diametral creep and axial elongation and hydrogen pick up. For PHWR700 Zr-2.5 Nb alloy tubes manufactured by forging route are being developed. The modified fabrication route involves forging to break the cast structure, followed by higher extrusion ratio and only one cold working step. Detailed microstructural examination has suggested that grain-size of these tubes are having thickness of 0.3–0.5 μm along radial direction and aspect ratio of 1:5:50::Radial:Transverse:Axial directions. The fracture, DHC and thermal creep behaviour of these tubes are being evaluated.

Additionally, heat-treated Zr-2.5 Nb alloy is also being developed for possible application as pressure tubes in AHWR. Heat-treated tubes are produced in quenched and aged condition. Quenching is carried out in two ways. For the RBMK (Russia) and Fugen (Japan) reactors water quenched and aged tubes are used whereas RBMK (Russia) reactors gas quenched and aged tubes (Coleman *et al* 2007; Singh *et al* 2009b) are also used. It may be noted that water quenching from two phase ($\alpha + \beta$) field results in transformation of high temperature β-phase to martensite (Coleman *et al* 2007) whereas gas quenching produces widmanstätten structure (Coleman *et al* 2007). Fabrication of both water quenched and gas quenched tubes poses

technological challenges and their final microstructural state influences the in-reactor performance of the pressure tubes (Coleman *et al* 2007). In order to control/mitigate dimensional changes during service, it is important to have a stable microstructure with respect to both thermal and irradiation exposure. A fine uniformly distributed equilibrium β_{Nb} (with high Nb content) is desired (Coleman *et al* 2007).

4. Boron-based control rod materials

Any nuclear fission reaction produces more neutrons than it consumes. Control elements containing materials which strongly absorb neutrons form an essential part of a nuclear reactor, to balance the neutrons for the chain reaction. Boron is one of the very few elements which qualify as control materials. The neutron absorption property of boron is mainly due to the presence of Boron-10 (B^{10}), which undergoes the main capture reaction:

$$_5B^{10} + _0n^1 \rightarrow _3Li^7 + _2He^4 + 2.6 \, \text{MeV}. \tag{3}$$
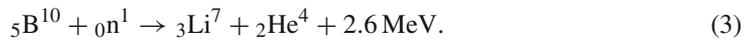
The cross section of this reaction varies from 3850 barns for thermal neutrons to a few barns for fast neutrons. Boron-10 is an excellent candidate for absorbing neutrons in thermal reactors. At higher energies, the cross section of most other elements becomes very small, where as that of B^{10} decreases monotonically with the energy and at higher neutron energies of >1 MeV also B^{10} exhibits sufficient absorption cross section values. The natural abundance of B^{10} isotope in boron is 19.8%, which can be enriched up to 99%. This makes the use of boron very attractive in the entire energy spectrum. The (n,α) reaction of B^{10} produces lithium and helium in their stable and non-radioactive forms. Boron carbide, due to its high boron content, chemical stability and refractory character, is extensively used as control rod material.

4.1 *Boron carbide*

For the construction of research reactor DHRUVA in the early eighties, efforts to develop indigenous production of neutron absorber materials were initiated at Bhabha Atomic Research Centre, Mumbai. Keeping in view the nature of Indian atomic energy program, boron-based neutron absorber materials was selected. Boron carbide was first produced by carbothermic reduction of boric acid in graphite resistance furnace. This material mixed with concrete or other sealants is used for shielding of neutrons at various locations in the reactor. A cermet named BORAL, a dispersion of fine boron carbide powder in aluminum matrix is produced by powder metallurgy and this cake is further shaped to sheet form by picture framing in aluminum and hot rolling. These sheets are effectively used as neutron shields in the reactor walls surrounding neutron beam holes and also in nuclear instruments. Silicon rubber mats with boron carbide dispersions are used as flexible sealant, in on line fuelling machines, nuclear material storage and transportation.

Boron carbide is usually prepared from its oxide by carbothermic or magnesiothermic reduction in the presence of carbon. Carbothermic reduction route was developed in BARC (Suri & Subramanian 2009; Suri *et al* 2010) using commercially available boric acid in place of boron trioxide as per the following reaction.

$$4H_3BO_3 + 7C \rightarrow B_4C + 6H_2O + 6CO. \tag{4}$$
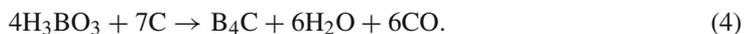
This process requires a temperature of >1500°C to start the formation of boron carbide and is generally carried out at temperatures in the range of 1900–2500°C.

The boron carbide lumps, as obtained from the furnace, varying in size up to 80–100 mm, are further crushed to small pieces in a jaw crusher and then to a fine powder in a pulveriser using multiple hammer heads lined with hardened manganese steel. This powder needs further purification to remove the small amounts of unreacted/partially reduced charge and the contaminants picked during the process of size reduction. The aqueous processing of boron carbide powder to remove the impurities is carried out in polypropylene lined fibre reinforced plastic tanks using hydrochloric acid for the dissolution of impurities and silica lined heaters for heating the solution. Agitation of the solid liquid mixture is affected by passing air under pressure through the bed. The flow sheet for the production of boron carbide powder from boric acid is given in figure 12. Graded powder mix filled in stainless steel tubes is used as control rods in Tarapur Atomic power Station (TAPS).

4.2 *Enriched boron carbide*

Research and development activities on enrichment of boron with ^{10}B isotope also started in the eighties by distillation process and through ion exchange media at BARC, later in the nineties relatively large columns of ion exchange facilities were set-up at IGCAR (Indira Gandhi Centre for Atomic Research) Kalpakkam. Today, both the processes have matured and production plants have been set-up by Heavy Water Board (A production unit of Department of Atomic Energy, India) at Talcher and Manuguru. Regular production of boron, enriched with ^{10}B isotope (∼65%) has commenced a year ago. Prototype fast breeder reactor, which is in the advanced stages of construction at Kalpakkam, needs high density enriched boron carbide pellets for control rods. Currently these pellets are under production at BARC using the enriched boron supplied by Heavy Water Board. The technology for the production of enriched boron carbide and consolidation to desired shape were developed at BARC and the processing steps are outlined below. In the first step, boron from boric acid enriched in ^{10}B is extracted by fused salt electrolytic process, followed by synthesis of boron carbide by reaction with carbon at a temperature of >1800°C. Boron carbide powder is further hot pressed in specially designed graphite dies to get dense boron carbide pellets.

Boric Acid + Carbon
↓
Mixing
↓
Carbothermic Reduction
↓
Boron carbide chunklets
↓
Jaw crushing
↓
Aqueous processing milling
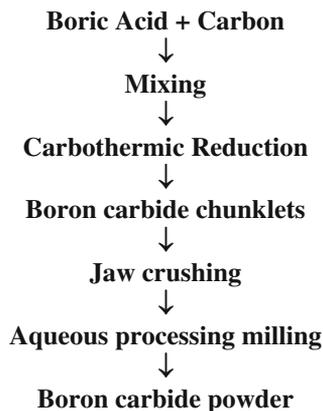↓
Boron carbide powder

Figure 12. Flowsheet for production of boron carbide powder (Suri *et al* 2010).

4.3 *Borides*

Boron carbide suffers from problems like pellet clad interaction, swelling and poor thermal conductivity. Borides of refractory metals with high melting points, good high temperature properties and higher thermal conductivities are preferred neutron absorbers for high temperature reactors. Materials Group, BARC has developed the production technology for TiB_2, ZrB_2, HfB_2 and CrB_2 and some of the compounds are used in advanced reactors under test. These compounds are produced by reaction between their respective oxides and boron carbide powders at high temperatures. As the reactions take place in solid state, close contact with the reactants is essential and to achieve this charge is made of compacts prepared under pressure from fine mixture of reacting powders. These borides are formed at temperatures $\sim$1400°C and further heated to a much higher temperature under a high vacuum of 10^{-5} m.bar to obtain pure products. Due to high melting points, covalent nature and low self-diffusion coefficients, it is a challenging task to sinter these materials and achieve high density compacts. Generally, hot pressing or hot isostatic pressing of powders is practiced to obtain high densities. Sinter additives are also often added to aid in consolidation and also to improve the properties of sintered parts. Silicides of Ti, Cr and Mo are excellent sinter additives to borides owing to their low melting points, high thermal conductivities, and thermal coefficients close to that of borides. These silicides also improve high temperature oxidation resistance of borides due to the formation of silica/borosilicate glass on the oxidized surface. Tetra and hexa borides of rare earths are excellent neutron absorbers and these materials could be used directly as powders without consolidation for neutron absorption even in FBRs. Experimental investigations were successfully carried out in collaboration with Central Electro Chemical Research Institute, Karaikudi, Tamil Nadu to obtain pure phase compounds of EuB_6, YB_6, NdB_6 and SmB_6. Fused salt electrolytic method was found suitable for synthesis of these rare earth borides. The data on synthesis of borides and conditions for consolidation are presented in tables 3 and 4 (Suri *et al* 2010).

It may be noted that synthesis of boron carbide and refractory metal borides requires a temperature of 1800°C. Though pure EuB_6 was obtained at 1700°C, the recovery was poor. Pure borides of rare earths could be conveniently produced at a lower temperature (900°C) by fused salt electrolytic process. Hot pressing and additives bring down the sintering temperature substantially and also the sintered compacts obtained have high densities and higher hardness values. For boron carbide and also for borides, densities close to theoretical values were obtained by hot pressing (Suri *et al* 2010).

Table 3. Conditions for synthesis of boron carbide and borides (Suri *et al* 2010).

S. No.	Compound synthesized	Charge composition	Temperature (°C)	Phases present
1	B_4C	B+C (B/C > 4)	1800	B_4C + Graphite
2	TiB_2	$TiO_2 + B_4C + C$	$\geq$ 1800	TiB_2 Pure
3	ZrB_2	$ZrO_2 + B_4C + C$	1800	ZrB_2
4	HfB_2	$HfO_2 + B_4C + C$	1825	HfB_2
5	CrB_2	$Cr_2O_3 + B_4C + C$	1700	CrB_2
7	EuB_6	$Eu_2O_3 + 3B_4C$	1400	EuB_6
8	YB_6	$Y_2O_3 + 3B_4C$	1700	$YB_6 + YB_4$
9	EuB_6	By Fused salt electrolysis	900	EuB_6
10	NdB_6	By Fused salt electrolysis	900	NdB_6
11	SmB_6	By Fused salt electrolysis	900	SmB_6

Table 4. Conditions for densification of boron carbide and refractory metal borides (Suri *et al* 2010).

Material	Sinter addition	Process parameters	D, %ρ_{th}	Hardness, GPa	Microstructure
B_4CD_{50}-0.5 μm	Nil	PS–2375°C	90	25	Coarse grains 50–120 μm
	5.0 % ZrO_2 D_{50}-<1 μm	PS–2275°C	93	32	Two phases <20 μm
	Nil	HP-1900°C	98	32	1–2 μm
TiB_2D_{50}-1.1 μm	20% $MoSi_2$	HP-1700°C	99	25	1–2 μm
	2.5% $TiSi_2$ D_{50}-15 μm	HP-1550°C	99	25	1–2 μm
	5% $CrSi_2$ D_{50}-18 μm	HP-1700°C	99	28	-
	2.5% CrB_2 D_{50}-4.8 μm	HP-1750°C	97	18	2–3 μm
ZrB_2D_{50}-2.0 μm	Nil	HP-1850°C	100	15	4 μm
	2.5% CrB_2 D_{50}-1.8 μm	HP-1750°C	100	17	2 μm
HfB_2D_{50}-2.2 μm	Nil	HP-1850°C	80	15	-
	5%$TiSi_2$ D_{50}-15 μm	HP-1650°C	95	23	-

PS- pressure less sintering, HP- hot pressing, D_{50}- mean particle diameter and D –density as fraction of theoretical density

5. Steels for fast and fusion reactors

5.1 *In-core materials*

Various stainless steels are used as structural materials in fast breeder reactors. The intense fast neutron (energy > 1 MeV) flux coupled with liquid sodium environment and the temperature range of 675 to 975 K makes stringent demands on the in-core structural materials, i.e., clad and wrapper materials. These materials need to have resistance to irradiation-induced swelling and irradiation embrittlement, sodium corrosion and a good creep resistance. For Prototype Fast Breeder Reactor (PFBR), the material for clad and wrapper tubes is 20% cold worked 14Cr-15Ni-Ti stabilized austenitic stainless steel called D9. For future cores where a burnup of 150,000 MWD/t is envisaged, a modified alloy D9I is being developed by IGCAR, Kalpakkam by changing the content of the minor elements such as Ti, Si and P which affect the void swelling of austenitic stainless steel strongly. The optimized contents for these elements are 0.25 wt.% titanium, 0.04 wt.% phosphorus and 0.75 wt.% silicon (Mathew *et al* 2009; Baldev Raj 2011).

For still higher target burnups, like 200,000 MWD/t, an oxide dispersion strengthened (ODS) ferritic martensitic steel of nominal composition (wt.%) Fe-0.11C-9Cr-2W-0.2Ti-0.35Y_2O_3 with the requisite creep strength is being developed by IGCAR in collaboration with International Advanced Research Centre for Powder Metallurgy and New Materials (ARCI), and Nuclear Fuel Complex (NFC), Hyderabad. The yttria particles in the final microstructure are of about 10 nm size. The production of components follows a complex powder metallurgy route starting from powders of steel and nanometer size yttria followed by hot and cold mechanical processing steps. The steel has a creep rupture strength which is much higher than the modified 9Cr-1Mo steel but less than that of alloy D9. It is being attempted to increase the creep rupture strength

Table 5. Chemical compositions of alloy D9, alloy D9I and F-M ODS steel (Mathew *et al* 2009).

| | Composition (wt%) | | |
| | | Steel | |
Element	D9 SS	D9I SS	F-M ODS
C	0.035–0.05	0.03–0.04	0.11–0.13
Cr	13.5–14.5	13.5–14.5	8.8–9.2
Ni	14.5–15.5	14.5–15.5	–
Mo	2.0–2.5	2.0–2.5	–
Mn	1.65–2.35	1.65–2.35	<0.04
Si	0.5–0.75	<0.25	–
N	<0.005 ppm	<0.01	<0.01
P	<0.02	<0.04	–
S	<0.01	<0.01	–
Ti	5 C–7.5 C	0.25–0.28	0.19–0.22
B	10–20 ppm	<0.005	–
W	–	–	1.9–2.0
Y_2O_3	–	–	0.32–0.35

of 9Cr-ODS steel by increasing the Y_2O_3 content and by refining the size of the particles. The presence of very fine yttria particles not only enhanced creep resistance but it also acts as a sink for irradiation defects and thereby helping in controlling swelling, which is undesirable. The nominal chemical compositions of alloy D9, alloy D9I and F-M ODS steel are given in table 5.

5.2 *Out-of-core structural materials*

The principal material for high temperature structural components of PFBR like reactor vessels and primary and secondary loops is nitrogen-alloyed low-carbon grade type 316 L (N) SS. These components have a design life of about 40 years during which the material experiences creep, low cycle fatigue (LCF) and creep-fatigue interaction. The indigenously developed 316L(N) SS plates and 316N SS electrodes have been found to have the LCF and long term creep properties assumed in the design of PFBR components.

In order to increase the design life of structural components of future sodium cooled fast reactors from 40 years to 60 years and beyond, work is under progress to develop a high nitrogen 316LN SS with superior tensile, creep and low cycle fatigue properties as compared to 316 L(N) SS containing 0.07 wt.% nitrogen. The effect of nitrogen on the creep behaviour of 316LN SS has been studied at nitrogen levels of 0.07, 0.11, 0.14 and 0.22 wt.% by keeping the rest of the composition unchanged. The carbon content in these heats was 0.03 wt.%. It has been established that the optimum level of nitrogen in 316LN SS is in the range 0.12–0.14 wt.% from consideration of creep rupture strength and ductility. Nitrogen dissolves to a larger extent than carbon in the matrix, reducing the stacking fault energy of the matrix and introducing stronger distortions in the lattice, leading to stronger solid solution hardening. Nitrogen also decreases the diffusivity of chromium in austenitic stainless steels leading to retardation in coarsening of $M_{23}C_6$ thereby retaining the advantages of carbide precipitation for longer durations (Mathew *et al* 2009).

Based on LCF tests in the range 300–873 K, on 316LN with 0.11, 0.14 and 0.22 wt.% N, it is found that beneficial effect of nitrogen on fatigue life is observed to be maximum in between

Table 6. Chemical compositions of 316 L(N) SS base metal, 316 N SS weld metal and 316 LN SS (Mathew *et al* 2009).

	Composition (wt%)		
	Material		
Element	SS 316L(N) base	SS 316 N weld	SS 316 LN base
C	0.02–0.03	0.045–0.055	0.02–0.03
Cr	17.0–18.0	18.0–19.0	17.0–18.0
Ni	12.0–12.5	11.0–12.0	12.0–12.5
Mo	2.3–2.7	1.9–2.2	2.3–2.5
Mn	1.6–2.0	1.2–1.8	1.6–2.0
Si	<0.5	0.4–0.7	<0.5
N	0.06–0.08	0.06–0.10	<0.14
P	<0.03	<0.025	<0.03
S	<0.01	<0.02	<0.01
Fe	Bal.	Bal.	Bal.

0.11–0.14 wt.% N at T > 673 K. The nominal chemical compositions of 316 L(N) SS base metal, 316 N SS weld metal and 316 LN SS are given in table 6.

5.3 *Steam generator materials*

Normalized and tempered Mod.9Cr-1Mo steel (9Cr-1MoVNb) used as the steam generator material in PFBR has a tempered martensitic structure. The role of V, Nb and N in this steel is to promote intragranular precipitation of highly stable V, Nb-carbonitrides (MX) particles on tempering and during creep exposure to achieve relatively high creep strength. Laves phase (Fe_2Mo), an intermetallic compound, is found to precipitate on grain and subgrain boundaries on thermal and creep exposures in the high-chromium ferritic steels containing Mo and W. The Laves phase precipitates are expected to decrease the solid solution strengthening but they increase the precipitation strengthening of the steels when they are fine in size. Intergranular precipitation of complex Cr(V,Nb)N particles called modified Z-phase is reported when this steel is given long-term high temperature thermal and creep exposures. They precipitate fine, but grow quickly by dissolving the beneficial MX types of precipitates to accelerate the recovery process of the steel. Long-term thermal and creep exposures decrease the steel's strength drastically due to Z-Phase.

Microstructural degradation and oxidation during low cycle fatigue were found to play a detrimental role on the fatigue life of Mod. 9 Cr -1 Mo steel. The component life was more adversely affected during compression hold conditions than during tension hold conditions. The thermal fatigue problems in steam generators in future FBRs may be alleviated through reduced section thickness and a modified material. A more creep-resistant version of Grade 92 steel is being developed for this purpose (Mathew *et al* 2009).

5.4 *Fusion reactor structural materials*

The chosen structural material for the breeding blankets for DEMO reactor and test blanket modules (TBMs) is ferritic martensitic steel. Ferritic martensitic steels possess a very good

dimensional stability under irradiation (swelling resistance), combined with better thermophysical and thermomechanical properties. 'Low activation' or 'reduced activation' ferritic martensitic steels (RAFMS) were developed to achieve a faster decay of induced radioactivity by reducing the alloying and impurity elements which contribute to radioactivity through transmutation. This reduces their cost of disposal after service: deep geological storage will not be required and shallow land burial will be enough.

RAFMS is obtained by replacing high activation elements in the modified 9Cr -1Mo ferritic martensitic steel like Mo and Nb with low activation elements like W and Ta, respectively. MX carbonitrides such as vanadium nitride or tantalum nitride impart strength by stabilizing the dislocation network, while tungsten provides solid solution strengthening. Double vacuum melting is done, to achieve defect-free homogenous and pure ingot. A fine-grained structure is achieved by hot working in a controlled range. The mechanical properties can be made more predictable by heat treatment at close temperature (Narayana Rao 2011).

6. Fusion reactor functional materials

6.1 *Lithium titanate*

India is a partner in the International Thermonuclear Experimental Reactor (ITER) programme. In a D-T fusion reactor, the important functions of breeder blanket material include breeding of tritium, converting the kinetic energy of fusion neutrons into heat, and finally, shielding the components surrounding the blanket from energetic neutrons as well as photons. Lithium-based oxide ceramics ($LiAlO_2$, Li_4SiO_4, Li_2ZrO_3 and Li_2TiO_3) have been considered as tritium breeder material due to their good thermal properties, especially high thermal conductivity, as well as satisfactory breeding characteristics. Among these ceramics, Li_2TiO_3 is considered as the candidate material because of its fairly good tritium release property and low activation characteristics. Key concepts related to the various fusion engineering issues and tritium breeding will be tested by the Test Blanket Module (TBM) titled Liquid Lead Lithium Cooled Blanket (LLCB). This TBM will use Lithium Titanate (Li_2TiO_3) pebbles as breeder material and Pb–Li alloys as coolant. Lithium in coolant would also breed tritium.

Two sol–gel based methods of producing these pebbles are under development in BARC: (a) production of Li_2TiO_3 powder and its consolidation by sintering into pebbles; and (b) direct production of Li_2TiO_3 pebbles and their densification by sintering.

In the first approach (Amit Sinha *et al* 2009), Li_2TiO_3 powder is prepared by a solid–liquid combustion synthesis using solid hydrous titania powder ($TiO_2.xH_2O$ where $x = 0.97$) and liquid $LiNO_3$ as the starting materials for titanium and lithium respectively. Work is under progress to produce Li_2TiO_3 granules by self-milling of Li_2TiO_3 powder in the presence of a binder (polyvinyl butyral). In one study, the granules so fabricated were sieved and subsequently sintered at 1200°C for 2 h. Figure 13 shows the appearance of the pebbles produced during this trial.

The second approach (Vittal Rao *et al* 2012) uses an Internal Gelation Process (IGP), a water-based sol–gel process, for the fabrication of high density Li_2TiO_3 pebbles using titanium oxychloride and $LiNO_3$ as raw materials. The precursor gel particles, produced by forcing the feed solution through an SS mesh of size 0.8 mm, are dried using azeotropic distillation of CCl_4. The dried pebbles are then sintered at 1100°C for 2 h to produce the final pebbles whose diameter is in the range 0.6–0.7 mm with aspect ratio in the range 0.98–1.02. Micrographs depicting the Li_2TiO_3 pebbles produced by this process are shown in figure 14.
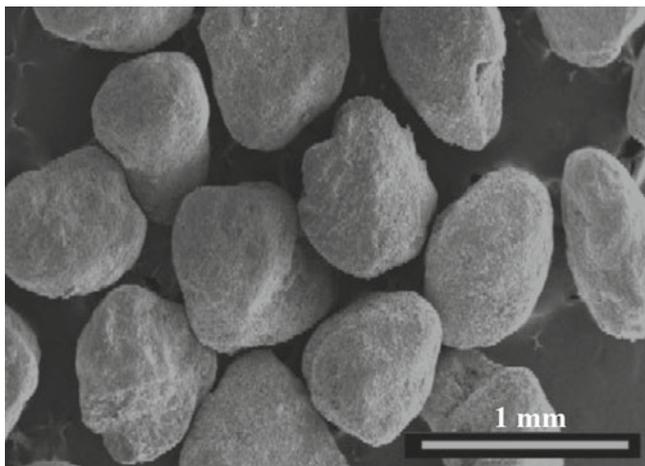
Figure 13. Li$_2$TiO$_3$ granules produced after sintering at 1200°C for 2 h.

6.2 *Pb–Li eutectic*

A liquid eutectic alloy Lead-17at% Lithium is considered as one of the most suitable Tritium breeder, neutron multiplier and coolant for fusion reactors. India's Lead–Lithium Ceramic Breeder (LLCB) TBM uses this alloy for these functions. For the successful integration of the TBM, several issues related to this alloy are being investigated. These concern the production, circulation by buoyancy flow and pump-driven flow, and corrosion of the structural materials in static and flowing eutectic.

6.2a *Production*:   The successful production of this eutectic is a major concern because of the large difference in densities of its two constituents, i.e., lead and lithium and also the prevalence
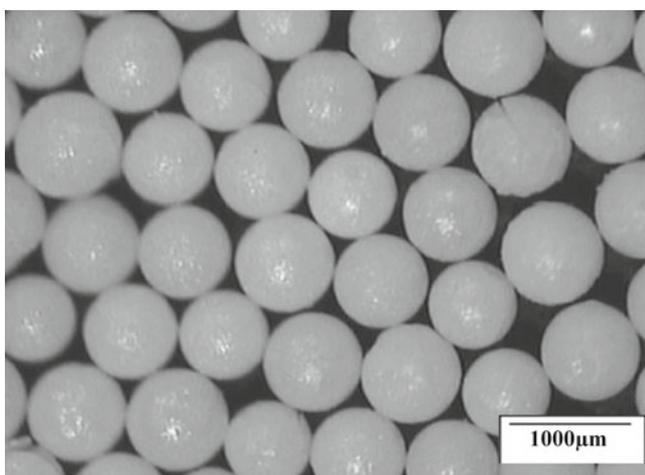

Figure 14. Li$_2$TiO$_3$ pebbles produced by internal gelation process followed by sintering at 1100°C for 2 h.

of Lead up to 83 at.% in the eutectic composition. To meet this challenge, a Lead–Lithium eutectic production facility that uses permanent magnet stirring technique has been designed and fabricated at BARC. The magnetic stirrer circulates and thoroughly mixes the alloy constituents in a specially designed reactor through the principle of electromagnetic induction. The set up has a production capacity of 4 kg of alloy which will be scaled up to higher capacities in future.

6.3 *Studies on the flow of eutectic*

6.3a *Development of instrumentation*: An electromagnetic induction pump based on permanent magnets has been designed and constructed with the aim of attaining high pressure heads and large flow rates as is required in case of heavy liquid metals such as Mercury, Lead and Lead-based eutectic alloys. The Pressure - Flow (P-Q) characteristics were generated with the help of a Mercury loop and were found comparable to that of a centrifugal pump. The pump has been operated successfully in forced circulation liquid metal loops for 2500 h continuously.

An electromagnetic flow meter has been developed to measure the liquid metal flow velocity in liquid metal loops. This is very important since flow velocity is a prime factor affecting liquid metal corrosion. The flow meter works on induction principle and is extremely sensitive to small velocity fluctuations. The working of such flow meter does not depend on the electrical conductivity of the liquid and was also found to be independent of temperature fluctuations. The calibration of the flow meter has been carried out in Mercury, for which a separate Mercury loop was designed and fabricated.

A 1.8 T electromagnet has been procured and installed for facilitating corrosion studies under magnetic field. The maximum magnetic flux of 1.8 T is obtained at a voltage of 700 V. The temperature of the magnetic coil assembly is controlled up to a maximum of 50°C with the help of cooling fans. It has been experimentally calculated that the increase in magnetic field causes a decrease in the average flow velocity in liquid metal in the loop. This can have significant effects on the corrosion phenomenon being studied.

6.3b *Buoyancy loops*: Preliminary experimentation with flowing Lead–Lithium eutectic was started in buoyancy driven loops that contained corrosion coupons of 9 Cr-1Mo steel placed inside. Such loops allow corrosion testing at variable velocities depending on the diameter or height of the loop. Earlier, vast operational experience had been obtained by running similar buoyancy loops on *Lead–Bismuth* eutectic for 10,000 h. The first buoyancy loop on *Lead–Lithium* eutectic has been run for 1500 h with a thermal gradient of 100°C maintained between the hot and cold legs. The results were useful in establishing the corrosion rate of P91 steel in Pb-17Li at low flow velocities like 6 cm/sec.

6.3c *Pump-driven loops*: Forced circulation liquid metal loop allows the variation of flow velocity over a wide range and corrosion testing can be carried out at higher velocities as expected in the fusion reactors. But the construction of such loops needs simultaneous development of some of the important components like the Electromagnetic Pump (EMP), Heat Exchanger, Recuperator, Test Section (to hold the corrosion samples), Cold trap, Flow meter, etc. Such loops have been developed for conducting corrosion studies of P91 material under liquid metals like lead–bismuth and lead lithium. They have been successfully operated for 1000 h of operation at liquid metal flow rates of around 30 l/m.

6.3d *Pump driven loop for corrosion testing under magnetic field*:   In the presence of a high magnetic field, the hydrodynamics of liquid metal flow change drastically and can influence the corrosion behaviour of structural materials in Pb-17Li. This is of prime importance with respect to blanket design and thus corrosion studies under magnetic fields are necessary. For this purpose, a forced circulation liquid metal loop was designed and fabricated to carry out corrosion experiment of 9Cr-1Mo steel (P91) in the presence of magnetic field. An Electromagnet providing a maximum flux of 1.8 T was installed at the test section kept at a temperature of 550°C. The loop was successfully operated with lead–lithium eutectic for 1000 h.

6.4 *Corrosion testing of structural materials in lead lithium eutectic*

6.4a *Static corrosion studies*:   Corrosion behaviour of Lead–Lithium eutectic towards various structural and functional materials has been investigated under static conditions at various temperatures. Corrosion of P91 in Pb–17Li has been analysed under static conditions and a suitable corrosion rate has been established. Corrosion of SS316L in Pb-17Li in the presence of various alloying elements like Nickel and Aluminum, have been studied up to 3200 h of exposure (Chakraborty *et al* 2012, 2013). Interaction of Silicon Carbide with static Pb-17Li is also being investigated at a temperature of 823 K. SiC will be used in the making of electrically insulating flow inserts along the TBM coolant channel.

6.4b *Rotating disc corrosion studies in flowing lead–lithium eutectic*:   Velocity of liquid metal flow is an important factor affecting the corrosion behaviour at a particular temperature. To study the effect of different flow velocities on the corrosion behaviour of Pb–17Li on different structural materials, rotating disc experiments have been planned. This set-up simulates various flow velocities as developed in a loop, though the construction and working are much simpler. For this purpose a magnetic coupling based rotating disc reactor has been indigenously designed and fabricated in-house and has been successfully commissioned. The initial experiment has been set-up to study the compatibility of P91 material at 550°C in Pb–17Li at a rotation speed of 700 RPM. The reactor has already clocked 1500 h of operation and is expected to continue till 5000 h.

7. Conclusion

In this article, the development of zirconium alloy components and its in-service degradation mechanisms, development of control rod materials, development and characterization of structural steels and functional materials for Indian nuclear power programme being pursued by Materials Group, BARC has been discussed. Production of hafnium-free nuclear grade zirconium has been mastered by only few countries including India. The challenges due to crystallographic anisotropy, limited solid solubility for alloying additions, anisotropic thermal expansion coefficient of zirconium and its susceptibility to aqueous corrosion, dimensional changes under irradiation, and embrittlement due to formation of hydrides and irradiation have been overcome to a great extent through technological development in zirconium extraction, modifying manufacturing practice for fabrication of different types of zirconium alloy components, developing life monitoring, life management tools and mechanistic modelling having predictive capability. Processes for the production of boron carbide powder, and its composites and enriched boron carbide pellets have been developed to cater to the control requirements of our thermal and fast reactors. Refractory metal borides are the latest addition to this family

of control materials, and economically viable processes for their production and consolidation have been developed. Fast reactors necessitate the mastery of different kinds of aggressive environments, like fast neutron flux, liquid sodium and higher temperatures, and the degradation resulting from these. The formulation of newer steels by fine-tuning the compositions to achieve the required performance is an on going process, leading to the successful indigenous development of D9I, ODS, SS 316 L(N), Mod. 9Cr-1Mo Steel and RAFMS at IGCAR, Kalpakkam. The fusion reactor materials are being developed, qualified and investigations on degradation due to interaction between the structural materials and eutectic are at an advanced stage of completion using facilities developed indigeneously. The work described in this article demonstrates critical role played by materials development in all the three stages of Indian nuclear power programme.

Acknowledgements

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