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Review Article

Materials Science and Technology: Research and Challenges in Nuclear Fission Power

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The performance and integrity of structural and functional materials are key issues in the safety and competitiveness of current and future nuclear fission reactors being developed for sustainable nuclear energy applications. The challenges towards development of nuclear structural materials arise due to the demanding hostile environments with respect to radiation, temperature, stress, etc., and requirements of total reliability and high performance over the long service life (say 60 years). A successful materials science research programme in nuclear industry has to take into account these challenges to improve the performance of materials and components in the emerging scenario of extending life of existing plants and realizing advanced reactors. In this study, material challenges associated with water reactors and fast breeder reactors (FBR) with focus on short-term and long-term strategies for materials development are considered. The materials in the existing and proposed future nuclear fission reactors are summarized along with a description of major material degradation mechanisms in different environments. The priority in the nuclear industry is to extend the life of reactors with robust safety features and sufficient cost-effectiveness, beyond forty to sixty years and from sixty to even one hundred years. The importance of modelling and developing predictive tools to estimate materials behaviour for effective computing of lifetime of nuclear reactor components is fast developing to cut down cost and time and also to enhance safety and confidence in existing and new systems. The future FBR technology relies heavily on advanced waste management and effective proliferation resistance. We review advanced reactor concepts of Generation IV forum and the new materials and technologies. Nuclear energy is not the right option for every country. Careful examination of the energy basket and commitment over a long period with effective mechanisms of safety governance is the key to make a decision to harness large amounts of nuclear energy. China, France, India, Russia, USA,UK, etc. are extremely committed to use large amounts of nuclear energy. Japan after the Fukushima accident, faces a challenge of public acceptance though the country has deep and rich expertise in nuclear technology and it is advantageous to produce low carbon power, on a sustained competitive basis from nuclear energy.

Keywords: Advanced Materials; Nuclear Reactors; Fission and Fusion; Challenges

Introduction

Nuclear power is a robust facilitator of energy security in countries with inadequate domestic fossil and renewable energy resources. Nuclear power is also a way to deliver low carbon energy integrated over the life cycle of an atom, to human civilization. There is incredible power in an atom. Disintegration of a single uranium atom produces several orders of magnitude more energy than burning of coal, oil or natural gas. However, nuclear power remains an under-appreciated marvel of modern technology. When we amplify the natural process of fission (by breeding), we can meet the entire energy need of the civilization for thousands of years with known resources of uranium and thorium. The comparison

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shows that for a 1000 MWe power plant, we may need ~160 t of natural uranium per year which can be brought in a single tractor trailer; but we may need ~2.6 million t of coal per year (i.e. 5 trains of 1400 t/day). For establishing solar or wind power, we need multifold more land compared to uranium and even coal-fired power plants. In the 1950s, the first commercial nuclear power station started operating; and today in the world, there are more than 400 commercial reactors based on nuclear fission and operating with 370,000 MWe total capacity (Raj *et al*., 2008). These plants are supplying 15% of the world's electricity. It is expected that the nuclear energy generation capacity will increase approximately to 1500 GWe in another 40 years (Raj *et al*., 2008). India has planned for a rapid increase in nuclear power capacity from the current installed capacity of 4120 MWe to 20,000 MWe by 2020 and 63,000 MWe by 2032 (WNA, 2014). Since awareness on the environmental issues resulting from coal-based power plants has increased, the clean nuclear energy will assume more importance in the coming decades (IAEA, 2004). Fully comprehending the setbacks from incidents such as Three Mile Island, Chernobyl and Fukushima, the nuclear industry is persistently striving to achieve higher standards of safety and reliability (WANO, 2006), especially for severe and black swan accidents (high risk, but extremely low probability). With additional conventional uranium fuel resources of 10.1 million t (Raj *et al*., 2008) that can last for 270 years with the current capacity of nuclear power, nuclear energy can be the synonym for sustainable energy in the future (WNA, 2005). The sustainability of nuclear energy, for thousand years and beyond, depends on advancement in two key technologies; closed fuel cycle technology for fast reactor and thorium fuel cycle technologies (UIC, 2007).

Future reactors are also being designed to work in a high temperature regime providing better thermal efficiency and multiple industrial uses. This enhancement can be achieved by advanced technologies such as high temperature gas-cooled reactors and accelerator-driven systems (ADS). ADS provides excellent resistance to proliferation by *in situ* incineration, closed fuel cycle, reducing nuclear waste, and next generation fuels and coolants with improved efficiency. Thus, nuclear industry no longer remains a mere producer of electricity; instead, it has resurged to symbolize the energy policy of the world (Raj *et al*., 2008). The new generation nuclear systems needs to be successfully implemented by developing advanced materials and their manufacturing technology in all the stages of nuclear energy systems such as ore refining, fuel fabrication, reactor technology, reprocessing and waste management. In synchrony with this, the materials research domain is undergoing a revolution responding with advanced materials which give priority to reduce nuclear power cost, that is, achieving higher burn-ups, longer life of reactors and less operational and maintenance costs. Fusion reactors, in the future, shall face many new challenges in materials and related technologies; however, these systems shall also build on large experience of fission, in particular, fast spectrum reactors (Stork *et al*., 2014 a, b).

Reactor Materials

Materials can be broadly classified into two main groups: For example (i) fuel assemblies, coolant channels and calendria tubes of pressurized heavy water reactor and (ii) clad and wrapper in fast reactor cores. A wide variety of materials are used as components of structures outside the core and inside the containment structures such as nuclear steam generation systems in water reactor. Conventional systems such as turbines and condensers constitute the rest of the plant components. (Fig. 1) (Dettmering, 2009). Inside the reactor core, the materials are subjected to demanding environments such as high

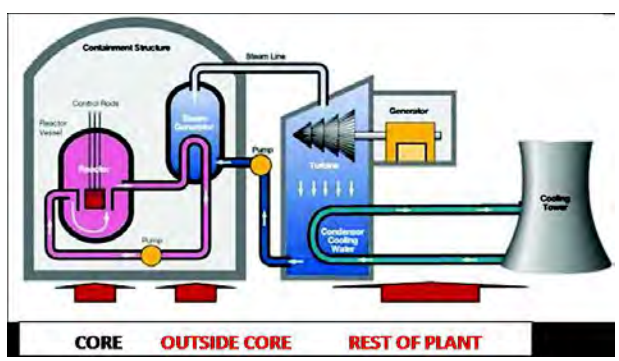

Fig. 1: Schematic of a nuclear power plant.
Source: Dettmering (2009)

temperature, temperature gradients, neutron irradiation, stress, etc. compared to out-of-core components, where temperature, stresses and corrosion are the key damage influencing parameters.

Thus, core materials need resistance to irradiation induced damages, excellent structural stability, excellent mechanical properties at high temperatures, compatibility with fuel/coolant/moderator and good fabricability and weldability. Table 1 shows the important criteria for selecting materials for components in thermal and fast reactors.

Based on the neutron energy regime of nuclear fuel fission, reactors are broadly classified into two types, thermal and fast reactors. The main criterion for choosing material for thermal reactor is low neutron absorption coefficient since fission is caused by neutrons with an average energy of ~0.025 eV. Zirconium-based alloys with a neutron absorption cross-section of 2×10^{-24} cm^2 are used for cladding. The candidate materials for pressure vessels and piping are carbon steels and low alloy steels or 12% Cr steels that are used for turbines and steam generators. Satisfactory performance of thermal reactors necessitates the extension of life from 40 to 60 to 100 years. In this context, small-sized specimen testing and advanced non-destructive evaluation coupled with modelling and simulation will enable us to obtain an in-depth knowledge of fracture mechanisms, micro-structural and structural degradations. In fast reactors where fission is caused by fast neutrons with an average energy of 0.2 to 0.5MeV, materials experience severe hostile environment with neutron flux of ~8×10^{15} neutrons/cm^2/s which is more than an order of magnitude higher than thermal reactors and high temperatures of 823 K compared to 573 K in thermal reactors. Fast reactors have a high target burn-up of 200 GWd/t compared to 80 GWd/t in

Table 1: Selection criteria of materials for components in thermal and fast reactors

Type of reactor	Component	Selection criteria
Thermal	Clad	Low neutron absorption coefficient Minimum interaction with the fuel pellet Compatible with the moderator/coolant Ability to withstand cladding stress due to fission gas release and thermal expansion Resistance to irradiation creep
	Structural	Low neutron absorption coefficient Minimum irradiation induced damage Minimum environment-induced changes such as chemical interaction with coolant and fission products, hydrogen damage, enhanced corrosion resistance under stress, irradiation and environment
	Pressure tubes	Minimum hydrogen damage such as hydrogen embrittlement, blistering and hydride cracking
Fast	Clad	Minimum dimensional changes due to void swelling and irradiation creep Reduced irradiation growth hardening and embrittlement Good compatibility with liquid sodium and fuel Stability of structure and mechanical properties
	Wrapper	Acceptable radiation damage and high temperature properties Good compatibility with sodium Good weldability and fabricability
	Structural	Good compatibility with liquid sodium Excellent structural stability high temperature mechanical properties Availability of design data Good weldability and fabricability Affordable cost

Source: Raj and Vijayalakshmi (2011) pressurized water thermal reactors. The selected materials should possess resistance to void swelling, irradiation creep and helium embrittlement and good compatibility with sodium, fuel and fission products. Thus, for a fast spectrum reactor, candidate materials for clad and wrapper are cold worked AISI 316 SS, 15% Cr-15%Ni-Ti stabilized stainless steel (Alloy D9) and ferritic steels. For structural components, 316 L and 316 LN stainless steels and for steam generator, modified 9 Cr-1Mo ferritic steels are currently chosen (Raj *et al.*, 2008).

Light Water Reactor Materials – Present Scenario

Zircaloy, an alloy based on zirconium, is the workhorse material employed for core components of thermal reactors. The light water-cooled reactors, especially boiling water reactors (BWR), use ceramic fuel pellets of UO_2 stacked in clad tubes made of Zr alloy tubes (3-4m long) that are grouped into fuel assemblies containing typically about 100 clad tubes arranged in a square array. Each assembly is encased in a square zirconium alloy tube, typically 12 cm on a side. They transfer heat to flowing water coolant and serve as the primary barrier to contain radioactive fission products. The control rod made of stainless steel tubes filled with boron carbide for neutron absorption are clustered into cruciform-shaped control blades and pass between assemblies (BARC, 2009). There are 700-800 fuel assemblies in BWRs and 300 fuel assemblies of larger diameter in pressurized water reactors (PWR) (Zinkle and Was, 2013). PWR and BWR cores operate 18-24 months between refueling with a core residence period of 304 fuel cycles and achieve cumulative burn-up levels of ~40-60 GWd/Mt of uranium. Non-fuel core components are core shroud (BWR), baffle-former assembly (PWR) and smaller components such as bolts, springs, support pins and clips. Out of core components are control rod drive mechanisms and housing, vessel head penetrations made of welded austenitic stainless steel and reactor pressure vessel. A typical BWR of 1960s genre designed and developed by GE (USA) and operated with success, meeting high levels of operational and safety standards by Nuclear Power Corporation of India is shown in Fig. 2.

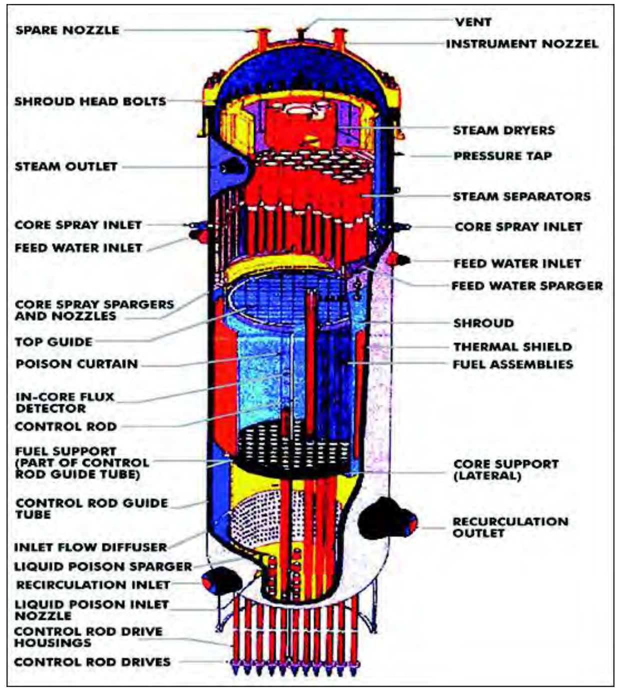

Fig. 2: Fuel assemblies and control rods of BWR (210 Mwe) at Tarapur, India. Source: BARC (2009)

Major pressure boundary components such as reactor pressure vessel (RPV), pressurizer, steam generator, steam lines, turbine and condenser are made of either low carbon or low alloyed steels. The RPV serves as a pressure barrier and containment for radioactive fission products and plays a key role in nuclear safety. RPV material is a ferritic steel with 1-2% Mn, 0.5-1% Ni, ~0.5% Mo and 0.15-0.4% Si (IAEA, 2009) with a wall thickness of ~20 cm. Austenitic stainless steels such as Types 304, 304L, 316, 316L, 321 and 347 dominate the core structural materials. Nickel based alloys are used for high strength components such as springs and fasteners. Though Alloy 600 was used for vessel penetrations and steam generator tubes, it is now replaced by Alloy 690 to overcome stress corrosion cracking susceptibility challenges.

The selection of Nickel based alloys and austenitic stainless steels for core internals and the steam generator tubes is driven by the need for good aqueous corrosion resistance at high temperature (Zinkle and Was, 2013). Condenser tubes are generally made of titanium and stainless steel.

Table 2: Reactor core environments for LWRs

System	Coolant	Pressure (MPa)	T_{in}/T_{out} (°C)	Neutron spectrum maximum dose (dpa)	Fuel	Electrochemical potential ECP
PWRs	Water-single phase	16	290/320	Thermal~80	UO_2(or MOX)	$<-500mV_{SHE}$
BWRs	Water-two phase	7	280/288	Thermal~7	UO_2(or MOX)	$150mV_{SHE}$

Source: Zinkle and Was (2013)

Table 2 shows that BWR environment has nobler electrochemical potential (ECP) (Zinkle and Was, 2013). This is due to the combination of boiling water in the core and radiolysis. However, PWRs operate at a lower potential because of the addition of hydrogen (~3 ppm) for scavenging radiolysis products. This lower ECP is better for stress corrosion cracking (SCC) and corrosion control. PWR primary water contains 1000 ppm boron as boric acid (H_3BO_3) for reactivity control along with 2-4 ppm Li as LiOH for pH control. Fuel and core components experience stress due to thermal expansion, high velocity water flow, residual stress due to welding, and stress due to radiation-induced volume expansion. All these challenges are overcome based on experience and continuing research (experiments and modelling). Typical zirconium alloy cladding materials used in BWR and PWR reactors are summarized in Table 3 (Zinkle and Was, 2013).

Pressurized Heavy Water Reactor (PHWR) Materials – Present Scenario

Pressurized Heavy Water Reactor (PHWR) of CANDU version uses deuterium, an isotope of hydrogen as moderator due to its low neutron absorption and natural uranium oxide as fuel. The major difference in materials used in this system as compared to LWRs is the use of Zr-Nb pressure tubes that house the Zircaloy-clad fuel and high pressure D_2O. These tubes fit into Zircaloy-4 calandria tubes that pass through thin-walled 304 stainless steel calandria vessel which also contains low temperature D_2O moderator. Thus, zirconium alloys play larger role as pressure boundary materials in PHWRs than LWRs.

A large number of zirconium alloys have been developed as the core structural materials. Efforts to increase the residence time of Zr-based components inside the reactor have resulted in development of Zircaloy-2, Zircaloy-4, Zr-Nb alloys and their variants. In the 1980s, advanced radiation-resistant materials were developed such as ZIRLO (ternary and quaternary alloys of Zr-Nb), M5, E110 and DX-D4(7). M5 alloy had excellent radiation and corrosion resistance, also hydriding, irradiation creep with negligible growth (0.7%) and achieved high burn-up values of 70 GWd/MtU. The duplex cladding DX-D4 has better mechanical and corrosion properties and radiation resistance up to a burn-up of 60 GWd/MtU. Attempts are made to enhance the burn-up to about ~80 GWd/MtU by improved fuel and structural materials. India has successfully developed and

Table 3: Typical commercial zirconium alloys used as cladding in PWRs and BWRs

Reactor type	Zr alloy composition	Thermo mechanical treatment
BWR	Zircaloy-2 (1.5% Sn-0.15% Fe-0.1% Cr-0.05% Ni)	Recrystallized
PWR	Zircaloy-4 (1.5%Sn-0.2%Fe-0.1%Cr)	Cold worked and stress relief anneal
PWR	ZIRLO (1-2% Nb-1% Sn-0.1% Fe)	Quench and temper/stress relief anneal
PWR	M5(1% Nb)	Recrystallized

Source: Zinkle and Was (2013)

matured PHWR technology in the commercial domain. India has capability to design, construct and operate upto 700 MWe PHWR indigenously.

1. Materials Degradation in Water Reactor Systems

Structural materials employed in nuclear reactors degrade in their properties under radiation and corrosive environment of operation. During service, more often, the degradation of materials initiates from the surface and the conditions at the surface will be entirely different from that of the bulk of the material. Hence, materials for use in nuclear environments are specified in terms of not only the chemical composition but with respect to microstructure, distribution and structure of grain boundaries, anisotropy, effects of cold work, heat treatment, residual stresses, etc. The surface condition including roughness, chemical state and cleanliness are also specified.

Nuclear fission reactions result in the release of different types of radiations, fission products, actinides and other products. There are five important bulk radiation effects on materials by neutrons such as radiation hardening and embrittlement; radiation-induced and radiation-modified solute aggregation and phase stability; irradiation creep; void swelling and helium embrittlement. Neutron irradiation at LWR-relevant conditions (523 to 623 K) also reduces fracture toughness of austenitic SS. This will be a serious concern in ferritic/martensitic steels as it can lead to radiation embrittlement of reactor pressure vessel (Zinkle and Was, 2013). At intermediate temperatures between 573 K and 673 K, radiation-induced solute segregation and modified precipitation, void swelling, irradiation creep and anisotropic growth can occur. Materials for nuclear energy systems that exhibit irradiation growth include graphite, zirconium, beryllium and other metals or alloys (Zinkle and Was, 2013). At high temperature (>0.5 T_M), helium produced from (n, α) reactions within materials diffuses into grain boundaries, where it can form large bubbles that weaken grain boundary strength. Dramatic reduction in the total elongation will cause helium embrittlement. Corrosion occurs in all the major systems exposed to a water environment, including the reactor core, steam generator, turbine, condenser and piping, valves and fittings. It occurs in a wide variety of alloys such as carbon and low alloy steels used in piping and turbine components, stainless steel used in core internals and primary flow circuits and the condenser, nickel based alloys in the steam generator and in reactor vessel penetrations and welds, and zirconium alloy fuel cladding (Zinkle and Was, 2013). As the plants age, the most important corrosion issues will be SCC and irradiation-assisted stress corrosion cracking (IASCC) and uniform corrosion.

Gamma rays can radiolyse water and create free radicals that raise corrosion potential and change water chemistry. This change in potential leads to a multitude of corrosion and SCC including irradiation-assisted phenomenon that affect the performance of structural materials. For core components of LWR that suffer from IASCC ferritic-martensitic materials with inherent radiation resistance is considered; and for radiation embrittlement problem of reactor pressure vessel in PWR, ferritic steels show better performance (Zinkle and Was, 2013).

In the last decade, light water fission reactors in the US contributed 90% average capacity factor, demonstrating very high reliability. However for extending the operating life time of these reactors, extensive R&D to investigate corrosion and neutron-induced material degradation phenomena is in progress. Fracture toughness data collected for Types 304 and 316 austenitic stainless steels in LWR conditions of 523-623 K clearly showed fracture toughness while approaching value near 50 MPa $m^{1/2}$ after 5-10 dpa (Pawel *et al*., 1996; Rowcliffe *et al*., 1998). Intensive investigations are completed on the possibility of neutron radiation-induced embrittlement of reactor pressure vessels (Odette and Nanstad, 2009). Long-term experiments confirmed that radiation-induced precipitation due to neutron irradiation is not limited to temperatures above 673 K, instead it can occur even at 573 K (Kenikand Busby, 2012). Research is also focused on delaying the onset of steady-state swelling regime by identifying the mechanism that extends low-swelling transient regime (Wolfer, 1984; Mansur and Lee, 1991). Though at high temperatures, recovery of radiation damage occurs due to annealing of lattice defects, high temperature helium embrittlement reduces upper operating temperature of materials in nuclear energy systems (Zinkle and Was, 2013).

2. Material Degradation in Indian PHWR Systems Calandria

Type 304L austentic stainless steel irradiated by fast neutrons at the calandria normal operating temperature of 60°C will experience an increase in both the yield and the ultimate strengths. This increase in strength initially is very rapid up to a fluence of approximately 5×10^{24} n.m^{-2}, $E > 1$ MeV. While the material becomes stronger, the ratio of the ultimate to yield strength decreases indicating that the irradiated material is less ductile. This leads to neutron irradiation embrittlement. The end shields are fabricated from Type 304L stainless steel and filled with carbon steel shielding balls. The fuelling tube sheet, end shield shell and lattice tubes are exposed to lower fluences than the calandria tube sheet and the neutron embrittlement in these components, therefore, is not a concern. The calandria tubes are manufactured from Zircaloy 2 and installed within the reactor in a near-fully annealed condition. In service, they are subjected to a high neutron flux and they consequently undergo irradiation strengthening and some loss of ductility.

The austenitic stainless steel type 304L of which the calandria and the end shields are made is susceptible to SCC in a chloride environment. An elevated temperature and the presence of oxygen tend to aggravate SCC of this material. During fabrication of the stainless steel (304L) calandria and the end shields, care is taken to limit chloride contamination of the material. By strict fabrication specification limit for chloride content in solvents and cleaners used during the course of manufacturing to 100 ppm and maintaining excellent purity of moderator and demineralized water, very low chloride condition is maintained and SCC prevented even in the presence of oxygen (Jain, 2009).

3. PHWR Coolant Channels

The coolant channel assembly of PHWRs mainly consists of pressure tubes, calandria tubes and garter spring spacers made of zirconium alloys and end fittings made of stainless steel grade-403. Heavy water of 573 K and pressure of 10 MPa circulates through pressure tubes to transport the heat generated by fission of UO_2 fuel kept in zircaloy-4 sheathed fuel bundles to the steam generator through carbon steel feeders, headers and associated interconnected piping. The pressure tubes are the most important components in PHWRs and undergo degradation due to continuous exposure to intense radiation, high temperature, pressure and corrosive environment. Intense radiation causes atomic defects and consequent point defects resulting in microstructural, physical and mechanical changes.

Material hardening, reduction in ductility, and dimensional changes such as axial elongation, diametrical expansion and wall thinning occurs. Advanced techniques such as BARC Reactor Coolant Inspection System (BARCIS) and non-intrusive vibration diagnostic technique (NDVT) have been developed for regular in-service inspections. Pressure tubes made of Zircaloy-2 used in earlier PHWRs contain ~0.05% nickel which promotes hydrogen absorption. Hydrogen in atomic and molecular form is generated by radiolysis of heavy water coolant. Free radicals generated in radiolysis comprises H^* (D*) and OH* (OD*), which on recombination produce molecules of H_2O_2, O_2 and H_2. Hydrogen absorbed by Zr^{-2} forms zirconium hydride. At lower temperatures such as 423 K, the solubility of hydrogen in zirconium is low and hence hydride formation above threshold level reduces stress-bearing capacity of pressure vessels and makes it brittle. In Canadian PHWR, sudden failure of pressure tubes is reported due to building up of hydrides.

The hydrogen picked up during service by the Zr alloys forms hydrides along a specific habit plane close to basal plane (Suri, 2013). The crystallographic texture formation of Zr alloys depends on degree of deformation, thermo-mechanical history and alloy composition. Deleterious effects of hydrides can be reduced by controlling the texture so that hydrides are precipitated parallel to hoop stress (Singh *et al.*, 2007). The other two important life limiting factors are excessive irradiation creep and growth controlled by optimum level of cold work and suitable annealing temperature. Zr-2.5% Nb has high strength, corrosion resistance and reduction in hydrogen pick-up rate (Suri, 2013). The presence of Nb promotes recombination of nascent hydrogen isotopes to molecular form. Thus, hydrogen escapes in the coolant.

A computer code HYCON-95 was developed to predict hydrogen pick up by Zr-2 tubes and used for life management of all Indian PHWRs. Based on HYCON results, coolant channel replacement was made with Zr-2.5 Nb, which has better mechanical properties, higher resistance to radiation induced deformations and very low pick up of hydrogen which eliminated hydriding-induced degradation in pressure tubes of PHWRs.

4. Primary Side Flow-Assisted Corrosion (FAC)

Primary heat transport (PHT) system operates at average temperatures of 566 K (220 MWe)/577 K (540 MWe) at the outlet ends of channels in PHWRs. The PHT pipelines made of carbon steel carry hot heavy water from the channel outlets to a common header and from there to steam generators (SGs). Similar pipes also carry heavy water from the cold leg of SGs to the channel inlets after heat transfer at an average temperature of 522 K (220 MWe)/533 K (540 MWe). A protective magnetite (Fe_3O_4) film is formed on the inside surfaces of the carbon steel pipelines by a process called hot-conditioning during pre-commissioning operation. This film continues to grow during reactor operation under alkaline water chemistry (pH 10-10.5) and dissolved oxygen less than 10 ppb. Solubility of magnetite in water at pH more than 9.8 increases with increase in temperature from 423 K to 573 K. The PHT feeder pipelines have a contoured geometry, and at locations where high velocities and high temperature ~573 K exists at the outlet PHT feeders, higher thickness loss of magnetite results from flow-assisted corrosion (FAC). Using improved carbon steel (0.2% w/w chromium addition) and strict maintenance of pH in a range of 10.1 to 10.5 of hot coolant heavy water effectively prevented FAC (Jain, 2009).

5. Steam Generator

Steam generators with Monel 400 tube material was used in earlier generations of PHWRs. These alloys underwent SCC under high dissolved oxygen concentrations in the coolant and also exhibited higher rate of general corrosion. This resulted in the release of cobalt-59 (impurity with nickel in alloy), which generated highly radioactive cobalt-60 on irradiation with the thermal neutrons. This created radiation hazard for personnel and thus Monel 400 was replaced with Inconel-600. However, inter-granular stress corrosion cracking (IGSCC) of Inconel-600 led to the selection of Inconel-800. The Inconel-800 has demonstrated good general corrosion resistance especially under high dissolved oxygen concentration in the coolant (>100 ppb) and IGSCC. Nickel content is 30% w/w in Incoloy-800 compared to 70% in Monel-400 and hence the cobalt-59 associated with this material is nearly absent.

Tube failures in several SGs of nuclear power reactors have occurred due to material degradation mechanisms such as wastage and denting. During SG operation, sludge deposition occurs on lower tube sheet leading to circulation only in upper parts. This leads to accumulation of sodium phosphate in the intermediate region of tube sheet promoting high general corrosion of Ni-based alloys resulting in thinning of tubes and this is called wastage. Replacement of sodium triphosphate dosing by all volatile treatment (AVT) comprising hydrazine hydrate and morpholine additions to feed water, to reduce oxygen concentration less than <10 ppb and increase pH to 9.5, prevented these corrosion problems.

Due to accelerated corrosion of the tube support plates of SG made of carbon steel, voluminous corrosion products accumulate in the area between SG tube and tube hole on the drilled support plate. The flow decrease causes rise in temperature, increased evaporation and concentration of acidic chlorides caused crevice corrosion and this autocatalytic corrosion process resulted in the concentration of chlorides in the range of thousands of ppm. The bulky corrosion products thus formed exerted stress on SG tubes causing denting of tubes, and also produced tensile stresses on the ID side of

SG tubes causing primary water stress corrosion cracking (PWSCC). The change of tube support material to stainless steel solved this problem (Jain, 2009).

Use of erosion resistant stainless steel in river water cooled condensers and titanium in seawater cooled condensers avoided condenser tube leakages and contamination of SG water and thus SG tube failures by under-deposit corrosion. Continuous or intermittent blow-down of SG water keeps the water chemistry parameters within permissible limits to avoid SG tube and turbine blade corrosion.

Primary water stress corrosion cracking has been one of the major mechanisms in steam generators or control rod drive mechanism nozzles in nuclear power plants (Kim and Hwang, 2008). Environmental barrier coatings are chosen to mitigate the problem or electrochemical corrosion potential control is adopted. Alternatively, mechanically enhancing surface with induced compressive stress through a technique such as shot peening is also considered as a possible method. While electroplating with Ni is useful, electroless nickel plating is considered better due to its economical nature and robustness to coat complex geometry with ease.

Pulled tube examinations are a very convenient way of gathering essential information to gain more knowledge about the corrosion process. Laboratory examination of few hundred tubes drawn out from a plant provides extensive data on secondary side cracking, corrosion location, orientation, surface extension, length, depth, density, morphology, etc.; deposits and oxides composition; leak rate of the cracks; burst pressure of the degraded segment; mechanical properties of segments with or without cracking. Systematic evaluation of the database would help in understanding the characterization of degradation. This requires extensive validation of the non-destructive examination techniques. Therefore, non-destructive testing (NDT) gadgets should be incorporated in those tubes experiencing corrosion in PWRs (Cattant, 1997).

Life extension of SGs and plant life management require extensive survey of the ageing undergone by several tubes. It is reported that in Alloy 800 tubes, boron precipitation at grain boundaries is attributed to ageing through operation. In addition, the effect of boron segregation on the integrity of Alloy 800 SG tubing needs further investigation (Lu *et al*., 2012)

Fast Breeder Reactors

Fast reactors operating at high temperatures require an effective coolant such as sodium with high melting point (~1123 K) at atmospheric pressure. There is no need for moderator or any pressurizing of the coolant. The Pu 239-based mixed oxide fuel core is submerged in liquid sodium pool and heat is removed by primary liquid sodium cooling loop which transfers energy to the intermediate liquid sodium cooling loop. This heat energy is used to produce steam in steam generator for producing steam to drive the turbine (Suri, 2013).

During 400 years of SFR operation, important material's issues emerged in terms of liquid–solid material interactions, irradiation enhance/assisted materials evolution and life extension issues from economic point of power generation.

Due to non-uniform temperature in sodium loops of fast breeder reactors (FBRs), alloy elements dissolve in the higher-temperature region, and dissolved elements are deposited in the lower-temperature region, particularly carbon whose super saturation level varies with temperature. The carbon present in steels plays an important role in maintaining the material's strength properties. Thus, considerable emphasis should be placed on the decarburization and carburization phenomena in sodium. In a bimetallic sodium circulation loop consisting of austenitic stainless and ferritic steels, because of the difference in carbon activity between the two materials, decarburization occurs in ferritic steel, which has higher carbon activity, whereas carburization occurs in austenitic stainless steel (Bharasi *et al*., 2012).

In addition, considering FBRs being under service at higher temperatures than light water reactors, it is necessary to understand the high temperature mechanical properties; specifically, creep and low cycle fatigue with strong interactions in terms of ratcheting or cyclic creep (Yoshida *et al*., 2012).

Fast Reactors – Materials Aspects

The core of the fast reactor consists of fuel subassemblies containing typically (U,Pu) mixed carbide or oxide fuel which are kept in a pool of liquid sodium. The heat transport system consists of primary sodium circuit, secondary sodium circuit and steam-water system. Structural materials chosen for sodium circuit components must possess adequate high temperature low cycle fatigue strength and creep strength, and should be compatible with liquid sodium coolant. Fuel clad and wrapper materials should be resistant to irradiation-induced swelling and embrittlement, sodium corrosion and possess adequate end-of-life creep strength ductility. Steam generator materials must have sufficient high-temperature low cycle fatigue and creep strength and freedom from stress corrosion cracking (both chloride and caustic environments) and resistance to sodium decarburization. Through-thickness ductility is an important consideration in the choice of material for the top shield consisting of roof slab, large rotatable plug, small rotatable plug and control plug (Mannan *et al*., 2003).

The subassembly of a fast reactor consists of a hexagonal wrapper tube which contains fuel pins filled with nuclear fuel pellets. A typical Indian 500 MWe FBR has 181 fuel subassemblies arranged in a triangular array and a fuel subassembly contains 217 helium bonded pins each of 6.6 mm outside diameter (Raj *et al*., 2006). The neutron flux levels in FBRs are about two orders of magnitude higher (~10^{15} n/$cm^2 s^{-1}$) than thermal reactors. For economic viability, the target burn-ups required are more than 20 atom% of heavy metal (200,000 MWd/t). Fuel clad tubes experience temperatures in the range of 673-973 K under steady state operating conditions and during transient conditions the temperature can rise to 1273 K. For target burn-up of 100,000 MWd/t, the maximum neutron dose is 85 dpa. Major loads experienced by fuel clad are the internal pressure due to accumulated fission gases (~5 MPa) and minor loads such as temperature gradients and irradiation-induced swelling gradients. The hexagonal sheath (hexcan) of the core subassembly experiences lower temperature range of 673-873 K and transient temperature of 1073 K. The peak neutron dose is similar (85 dpa) and the load is the internal pressure of sodium coolant (~0.6 MPa).

In 1970s, stainless steels (SS) and nickel-based alloys with excellent properties at high temperature were evaluated for applications in the core of fast reactors (Mannan *et al*., 2003). Since, nickel-based alloys under irradiation exhibited helium embrittlement, three variants of steels such as 316SS and D9 (Ti-modified 15Ni-15Cr austenitic steels), 9-12 Cr-based ferritic steels and the oxide dispersant-strengthened (ODS) advanced ferritic steels were developed.

In fast reactors, void swelling and irradiation creep are the two major issues regarding materials. Void swelling refers to dimensional increase (Fig. 3A) (Garner, 1967) of the components due to condensation of vacancies into voids (Fig. 3B) (Cawthorne and Fulton, 1967). The swelling and irradiation creep susceptibility is measured as the increase in dimensions with increasing dose or stress (Fig. 3C&D) (Seren*et al*., 1992; Tolozko and Garner, 2004; Raj and Vijayalakshmi, 2011, Raj *et al*., 2008).

For different types of cold-worked stainless steels, the percentage change in diameter of the material with irradiation dose (dpa) of neutrons is

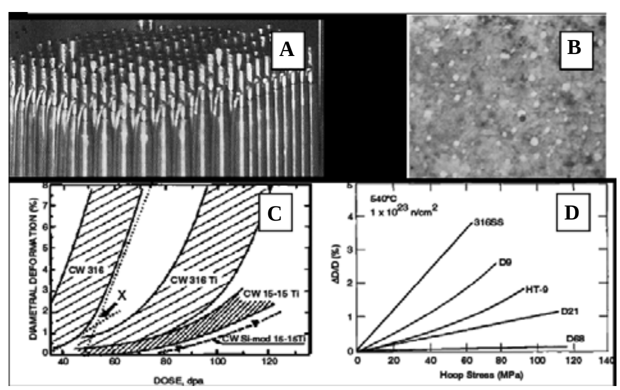

Fig. 3: Fast reactor clad material behaviour, A: dimensional change in the fuel assembly due to swelling and irradiation creep; B: Electron micrograph (60,000X) of voids (~0.5 µm) in irradiated 316 SS material; C: percentage change in the diameter of the material with irradiation dose for different cold-worked stainless steels and D: creep behaviour of candidate materials. Source: a (Garner, 1994); b (Cawthorne and Fulton 1967); c & d (Seren 1992; Tolozko and Garner, 2004)

depicted in Fig. 3c. The threshold dose is represented as the point of intersection X between the two linear portions of the curve. Irradiation creep refers to the permanent deformation of the material, leading eventually to fracture under combined effects of high temperature, stress and irradiation. Fig. 3d shows the creep behaviour of candidate materials such as D9, 316 SS, ferritic steel (HT-9) and nickel-based alloys (D21 and D68). With increasing hoop stress, the percentage diametrical strain was found to increase. These studies confirmed that the high-temperature creep properties of D9 were superior and the threshold dose was double compared to 316 SS (Latha *et al*., 2003).

The main objective was to increase the capability of materials to withstand high fuel burn-up. The trend in the development of radiation resistant 300 series austenitic stainless steel was to increase nickel content, decrease chromium content and identify roles of solute elements such as Ti, Si, P, Nb, B and carbon for excellent void swelling resistance. Thus, the advanced core materials, 20% cold-worked D9 alloy was developed. Further improvements of D9 like D9I were achieved by modifying minor alloying elements such as Ti, P, Si and B. These alloying elements altered behaviour of the fcc matrix and the interface of the newly formed precipitates that annihilated the radiation-induced defects. Oversized elements such as Ti, P, Si and B bind with vacancies and reduce swelling. Phosphide precipitation at high temperatures occurs, and at the interface between phosphides and matrix, annihilation of point, defects occurred which reduced swelling. Boron reduces mobility of carbon and nitrogen and binds to them, which enables fcc matrix to retain beneficial elements such as Ni, Mo, Si and Nb, and suppress the deleterious mechanism called solid solution decay. Oversized precipitates such asTiC-trapped vacancies and lattice strains around the precipitates are responsible for the superior properties of D9 (Fig. 4) (Divakar *et al*., 2003).Hence, D9 alloy has been selected as clad material in FBRs.

The fundamental difference in the behaviour of solutes and point defects in bcc lattice makes the ferritic steel superior to radiation damage. They can withstand fluences up to 180 dpa compared to ~ 100 dpa for D9 alloy and 45 dpa for 316 SS. Hence 9Cr-1Mo or 12Cr-1Mo ferritic steel are the candidate materials for wrapper in future sodium-cooled fast reactors. The maximum achievable burn-up has increased from 30 to 200 dpa which has shifted the focus of core component applications from austenitic stainless steel to ferritic steel. The advantages of ferritic steels are lower thermal expansion, higher thermal conductivity, better compatibility with liquid sodium than austenitic SS. Thus, creep-resistant 9-12 Cr ferritic/martensitic steels are candidate materials for core (clad, wrapper and ducts) and out-of-core applications such as sodium storage tank, piping and steam generators in fast spectrum reactor systems. The major disadvantage of these steels is deterioration of creep properties above 823 K and this has been overcome by developing oxide dispersion-strengthened ferritic-martensitic steels (ODS) (Ukai *et al*., 1993). During development of new variant ferritic steels, irradiation embrittlement, inferior high-temperature mechanical properties and Type IV cracking in their welds are observed. Under reactor exposure conditions, ferritic steels undergo microstructural changes (formation of secondary phases such as G-phase, M_6C and χ-phase) that lead to irradiation hardening, creep and embrittlement. By optimizing Cr content, 9Cr and 12Cr, strict control of tramp elements P, Pb, Sb, S and Sn (below 50 ppm), and by grain boundary engineering, ferritic steels exhibited

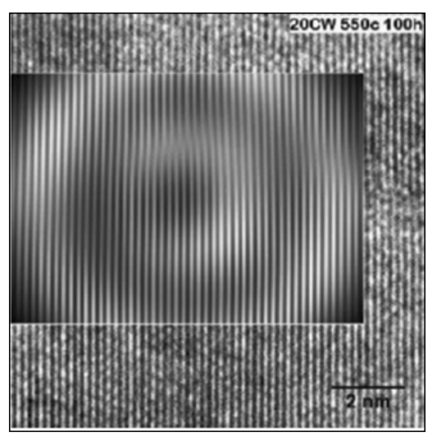

Fig. 4: High resolution transmission electron micrograph of 20% cold-worked D9, aged at 823 K for 100 h; the inset showing fringes that provide information on lattice strains around TiC precipitates. Source: Divakar *et al*., 2003

resistance to embrittlement. Grain boundary engineering involves enhancing low energy-coincident site lattice (CSL) boundaries in the steel and reducing the connectivity of the crack-resistant high angle boundaries. The operating temperatures have to be limited around 773K due to irradiation creep. Hence, ferritic steels are preferred in wrapper applications over clad tubes in oxide fueled fast reactors. The limitations of ferritic steel can be overcome for increased burn-up of FBRs with 100 years as lifetime at an operating temperature of 973K by development of oxide dispersion-strengthened ferritic-martensitic steels (Raj and Vijayalakshmi, 2010).

Reactor Assembly

The reactor assembly consists of core, grid plate, core support structure, main vessel, safety vessel, top shields and absorber rod drive mechanism. The inlet sodium temperature in the primary pool is 670 K and the mean core outlet temperature is about 820 K during normal operation and 923 K during transient conditions. The environment of operation is liquid sodium or aerosol of argon with sodium vapour or nitrogen gas. Except for grid plate near core which experiences an irradiation dose of 1 dpa in 40 years of design life, for all other components, irradiation is not a consideration. Austenitic stainless steels are chosen as the major structural material in view of their adequate high temperature mechanical properties, compatibility with liquid sodium coolant, good weldability, availability of design data, good irradiation resistance and vast satisfactory experience from sodium cooled reactors. Designers of FBRs prefer monometallic construction for liquid sodium systems to avoid interstitial element transfer (carbon in particular) through liquid sodium due to difference in thermodynamic activity in a bimetallic system. Localized corrosion of SS is absent since surface is clean in sodium (no passive film) and electrochemical reaction is not possible. However, mass transfer of metallic elements in SS can take place under the influence of non-metallic impurities in liquid sodium such as oxygen and carbon leading to formation of sodium chromite, carburization and decarburization which can influence mechanical properties. Type 316LN SS has been chosen for structural components of reactor assembly, other than the core components, operating at temperatures above 700 K; while 304LN SS is the choice for components operating at lower temperatures (Garner, 1994).

Welding is extensively employed in the fabrication of FBR components; and weld metal cracking and heat-affected zone cracking are major concerns in stainless steel welding. Weld metal cracking was controlled by optimizing composition of welding consumables (carbon 0.045 to 0.055 wt%, Nitrogen 0.06 to 0.1 wt%; ferrite number (3 to 7 FN)). Heat-affected zone cracking was controlled by specifying lower limits of P (0.025), S (0.02), Si (0.4-0.7), B (20 ppm), Ti and Nb (Ti+Nb+Ta= 0.1) for base metal (Garner, 1994).

In PFBR, the SG is a vertical, countercurrent shell-and-tube-type heat exchanger with sodium on shell side, flowing from top to bottom and water/steam on tube side. The high reactivity of sodium with water makes the SG a key component in determining the efficient running of the plant and demand high integrity of SG. The SG material should meet requirements of high temperature mechanical properties such as creep and low cycle fatigue, resistance to loss of carbon to liquid sodium (reduction in strength), resistance to wastage (small leaks lead to sodium–water reaction) and resistance to SCC in sodium and water media. The sodium inlet and steam outlet temperatures for PFBR are 798 K and 766 K, respectively. Susceptibility to aqueous SCC in chloride and caustic environments ruled out austenitic SS and Alloy 800. Modified 9Cr-1Mo steel with strictly controlled composition with respect to lower limits of residual elements (S (0.01 max), P (0.02 max) and Si (0.2-0.5)) was selected as the SG material with improved weldability, reduced inclusion content and high degree of cleanliness. Studies showed that Mod 9Cr-1Mo steel does not exhibit drastic reduction in creep strength at longer duration due to microstructural instability and this is the most important factor that favoured the selection (Mannan *et al*., 2003). This material also exhibited higher continuous cycling low cycle fatigue resistance than plain 9Cr-1Mo (Choudhary *et al*., 1991).

In out-of-core applications, the major thrust is to enhance the lifetime of materials up to 100 years.

A number of techniques such as computational methods based on plant history, visual observation and dimensional measurements, non-destructive methods, microscopy of replicas, *in situ* microscopy, biopsy-mechanical property evaluation of service exposed samples, etc. have been developed for life prediction of materials (Raj and Vijayalakshmi, 2010). Different NDT techniques such as fluorescent DP test for coarse surface flaws, X-ray radiography and ultrasonic testing for cavities/blow holes cast defects in bulk, ultrasound acoustic microscopy and laser scan microscopy for surface imaging, eddy current microscopy for visualization of electric and magnetic properties, Barkhausen noise and X-ray diffraction for residual stresses, IR imaging for thickness changes and cavitation damage has been developed for inspection of components in estimating the residual life (Raj and Vijayalakshmi, 2010). Operating temperature data is needed to assess damage and a phase evolution diagram (PED) has been developed to estimate the mean metal temperature. The change in the concentration of carbon excess of saturation limit in ferrite called supersaturation of ferrite with ageing time at chosen temperature, in addition to phase-fields of different metastable phases is depicted in PED of 9Cr-1Mo steel (Fig. 5) (Raj and Vijayalakshmi, 2010).

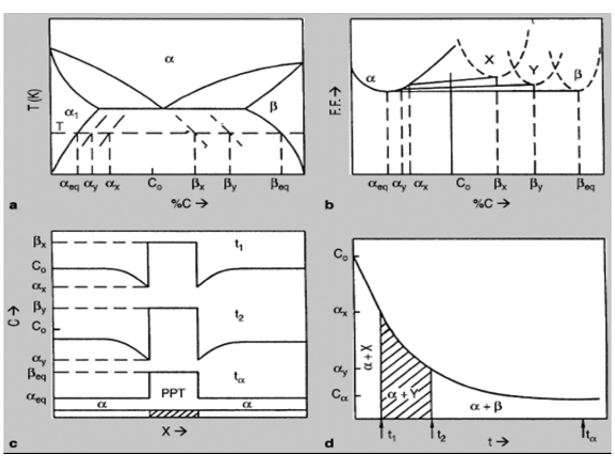

Fig. 5: Phase evolution diagram of 9Cr-1Mo steel at 1023 K: (a) schematic binary phase diagram, (b) free energy vs composition for co-existing phases, (c) profile of solute concentration near a secondary phase and (d) PED. Source: Raj and Vijayalakshmi (2010)

The welding consumable for modified 9Cr-1Mo steel has matching composition with minor modifications for Ni, Mn, Nb, V and N. There are two major limitations in the high-temperature performance of weldments inferritic steels such as Type IV cracking in creep-loaded weldments and formation of hard zone in dissimilar joints. The fine-grained intercritical zone of ferrite and formation of Z-phase (brittle nitrides of chromium) concomitant with the dissolution of MC carbonitrides cause Type IV failure of creep-loaded weldments of ferritic steels. At the dissimilar joints of austenitic SS structural materials and ferritic steel, diffusion of carbon leads to hard zone formation. Type IV cracking is reduced by adding boron 0.01% and reducing nitrogen to 0.002%. Boron strengthens grain boundary and combines with $M_{23}C_6$ for reducing creep rate, lowering nitrogen content reduces formation of Z-phase.

Trimetallic Transition Joint

The main structural and piping material austenitic 316LN SS cannot be directly welded to steam generator material made of modified 9Cr-1Mo material as large difference exists in thermal expansion coefficients, creep strength and carbon migration between them leading to failure. Hence, a trimetallic joint configuration consists of an Alloy 800 intermittent piece welded to 316LN SS on one side and to modified 9Cr-1Mo on the other side. For welding Alloy 800 to modified 9Cr-1Mo, Inconel 82/182 welding consumable was recommended and for welding to 316LN SS, 16-8-2 filler wire was selected (Mannan *et al.*, 2003).

Top Shield (Roof Slab)

Roof slab along with rotating plugs and control plugs forms the top cover of the main vessel, which provides biological and thermal shielding and acts as support for main vessel, pumps, intermediate heat exchanger (IHX), decay heat exchanger (DHX), etc. The mechanical load on roof slab is very high and temperature range experienced will be 373-393 K during normal operation and in the event of loss of cooling, temperature can go upto 473 K. The neutron flux experienced is also low (10^5 n/m^{2}s^{-1}). Carbon steel material A48P2 with good mechanical strength in the temperature range of 298–493 K and good weldability was selected for this application (Mannan *et al*., 2003).

Safety Grade Decay Heat Removal System

The safety grade decay heat removal (SGDHR) system consists of DHX, sodium to air heat exchanger (AHX) and piping connecting DHX and AHX. Since the material is susceptible to corrosion due to the humid chloride environment in the air, corrosion resistant modified 9Cr-1 Mo was selected for tubes and AISI 409SS as fin material (Mannan *et al*., 2003).

Fast Reactors – Short-Term Strategies

In fast reactors, improvement in thermal efficiency is an aspiration. The outlet temperature of the coolant should be increased from the present 823 K to about 1123 K (Raj *et al*., 2008). New variants in coolants such as helium gas and lead-based systems including Pb-Bi need to be evaluated and ferritic steels with better high temperature (>823 K), creep behaviour and better radiation resistance need to be developed. R&D efforts in strengthening the steel using 5 nm particles of yttria oxide dispersion strengthened (ODS) ferritic steels. Fig. 6 (Raj *et al*., 2013) shows the distribution of nano-sized yttria particles dispersed in ferritic steel and they are capable of withstanding 923 K up to a burn-up of 200 dpa with improved creep properties. Fuel clad tubes are fabricated from ODS alloys through powder metallurgy route (Raj *et al*., 2013; Murthy and Charit, 2008). Then, it is also essential to demonstrate dimensional accuracy during fabrication of clad and joining with end plug for wider commercial use. It is also important to generate an engineering database and validate performance and codification as part of materials system engineering technology. Dissolution resistant clad tubes in reprocessing and evolution of microstructures during reactor core residence, validation of high burn-up performance, etc. remain key challenges to be studied and mastered.

Materials for Fuel Cycle: Present Status and Short-Term Strategies

The nuclear power programme includes two options of fuel cycling. The fuel cycle is referred to as open fuel cycle (once through fuel cycle) if the spent fuel is not reprocessed. In the open fuel cycle option, the spent fuel is considered as waste and safely deposited in deep geological repositories. If the spent fuel is reprocessed and reused, it is referred to as closed fuel cycle. In the closed fuel cycle (Fig. 7) option, reprocessing of spent fuel is adopted for recovering the fissile and fertile elements and reusing them in the reactor. Closing the fuel cycle has an added advantage of minimizing the high level waste by separating and isolating the long-lived isotopes along with recovering extra energy from the original fuel. The storage time of nuclear waste can be reduced from millions of years to thousands of years and the volume of the waste can also be decreased by a factor of 4 if we adopt closed fuel cycle. From the spent fuel, the fertile materials are isolated and reused by converting to fissile material in fast reactors and this improves nuclear fuel efficiency.

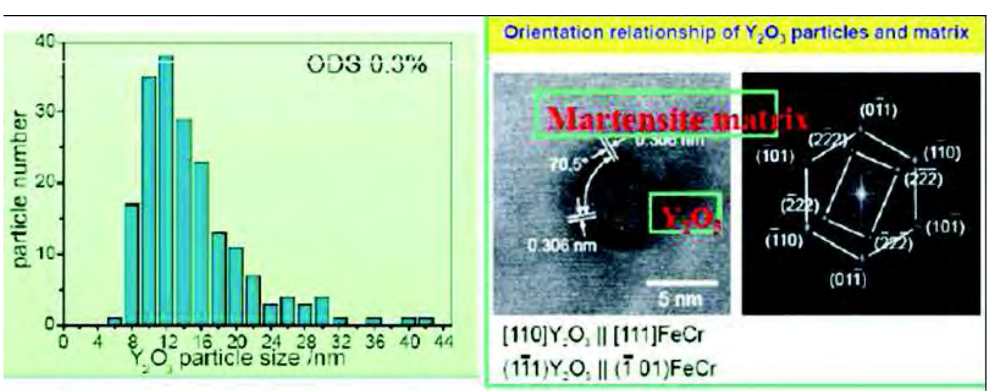

Fig. 6: Y_2O_3 particle size distribution in oxide dispersion strengthened steels and transmission electron micrograph showing orientation relationship. Source: Raj *et al.* (2013)

Fig. 7: Two fuel cycle options in nuclear programme. Source: IAEA (2009)

Table 4 shows the materials used for back-end technologies of reprocessing and waste management and the selection criteria which are entirely different from that of the reactors.

Aqueous reprocessing involves recovery of plutonium and uranium by extraction-PUREX process. Various components in the reprocessing plant are exposed to nitric acid and hence the materials need good corrosion resistance. AISI Type 304LSS was selected for the pipe and container materials due to good corrosion resistance. However, the presence of oxidizing species such as Fe(III), Pu(IV) and possibly Cr(VI) in nitric acid increases the oxidizing power causing severe intergranular corrosion even when SS is not sensitized. To combat corrosion, nitric acid grade (NAG) steel was developed (Mudali *et al*., 1993). Highly boiling and concentrated nitric acid led to the replacement of NAG SS with Grade 2 Ti material. The presence of Ti^{4+} ions inhibited Ti corrosion and presence of other oxidizing species did not affect Ti. An alternative material Ti-5Ta-1.8Nb has been developed with five times higher corrosion resistance than Ti and Ti-5Ta alloys. These alloys are also complemented with zirconium for dissolver vessels. The superior corrosion resistance of Zr-4 in both wrought and welded conditions in comparison to CP-Ti, Ti-5% Ta and Ti-5%Ta-1.8%Nb in 11.5 M HNO_3 has been established and considerable progress has been made in the dissimilar joining of Zr-4 to 304L SS (Mudali *et al*., 2013). Enhancement of the lifetime of reactors to 100 years has been planned and life of reprocessing plants also needs to be extended for which development of better reprocessing materials is a must.

Highly radioactive waste solution is finally immobilized in matrixes and hence matrix material should be stable in geological repositories for approximately 1,000,000 years by which time the radioactivity will diminish to natural level (Raj and Mudali, 2006). Borosilicate glass is used to vitrify high level waste (HLW) with higher radioactivity, packed into Cr-Ni steel canisters and disposed in rock salt formations. Research is in progress to develop several other ceramic matrixes that have higher chemical durability, mechanical integrity, thermal stability and can hold higher proportion of fission products or actinides. The matrix should remain stable for several thousands of years (Joseph *et al*., 2011). Borosilicates

Table 4: Selection criteria of materials for back-end technologies

Back-end Technology	Conventional materials	Selection criteria
Fuel reprocessing	Type 304L SS, nitric acid grade 304L SS, Ti and alloys, zirconium alloys, boron-coated SS	Stability against radiation damage. Corrosion resistance in boiling nitric acid. Necessity to remain sub-critical throughout the reprocessing
Waste management	Immobilization in borosilicate glass	Ability for high waste loadings, chemical durability, mechanical integrity, thermal stability. Incorporate many waste elements
	Vitrification in melter pots: Ni-base alloys	Ability to withstand high temperature. Radiation resistant for long time
	High-level waste canisters and over packs: copper, iron, SS, Ti alloys, Ni-base alloys	Excellent resistance to radiation, high temperature, and gradients and chemical compatibility interim shortage and permanent disposal, free from failure for long time

have compatibility problems with chemically heterogeneous waste for which glass ceramics are being developed. Synroc is an advanced ceramic with multiphases, and is developed to immobilize various forms of intermediate- and high-level waste. This titanate-based ceramic is made from several natural minerals such as zirconalite (calcium zirconium titanate), hollandite (barium aluminum titanate), and calcium titanate and titanium oxides. The advantages of synroc include enhanced durability over wider geological time frames; ability to incorporate into their crystal structures nearly all the elements present in HLW; no undesirable phase-separation reactions and robust chemical, physical and thermal properties (Raj *et al*., 2006).

The vitrified waste products will be cast and after interim storage, will be permanently disposed in a geological repository. Hence, the container material for vitrification should have a failure-free lifetime during all these stages. For additional protection against radionuclide mobilization, corrosion resistant packaging materials such as Ti 99.8-Pd, Hastelloy C-4, etc. were investigated and Ti-Pd alloy exhibited excellent corrosion resistance under salt brine conditions, temperature upto 473 K and gamma radiation of 10^3 Gy/h. The canister material also needs high corrosion resistance to geological environments containing chloride environments. Thus, the nitrogen-added stainless steels with higher corrosion resistance to chloride environments is developed which showed superior IGC resistance for 0.132% N and 0.193% nitrogen containing Type 304LN SS. Results suggest the suitability of this alloy in nitric acid and chloride containing environments of reprocessing and waste management plants (Parvathavarthini *et al*., 2012).

The proposed use of metallic fuel as fast reactor fuel introduces complications in the reprocessing routes and compatible materials. Requirements may vary for thorium fuel cycle also. Metallic fuels are best reprocessed by pyro-chemical processes with the high-temperature electrochemical route (Nagarajan *et al*., 2010). In the pyrochemical process, the spent fuel is electrolytically separated into reusable product and waste stream using high temperature molten salt electrolytes. This technique involves highly corrosive environment of molten LiCl-KCl salts. Thus, a new range of corrosion resistant coatings, graphite crucibles with ceramic oxide coatings of zirconia or alumina and refractory container materials are being developed (Mudali *et al*., 2011). Newer materials are also required for disposal of salt and solid waste generated by pyrochemical reprocessing. By melting solid metallic clad waste along with zirconium, metallic waste form is developed for geological disposal (Bairi *et al*., 2012). Thorium fuel reprocessing is being done in 13 M nitric acid using fluorides at relatively high concentrations as catalyst and aluminum nitrate to mitigate fluoride-related corrosion of Type 304L SS dissolver vessel. Studies on improvement of thorium dissolution process for reprocessing applications (Srinivas *et al*., 2012) could achieve high temperature sintered thoria pellets dissolution reactions in the absence of aluminum nitrate and with reduced fluoride content of 0.005-0.01 M instead of 0.3 M by changing the method of addition of the fluoride catalyst.

Surface Engineering of Materials for FBR Programme

Type 316LN SS used as structural material in PFBR operating at temperatures above 673 K is exposed to flowing sodium which removes the protective oxide film leading to self-welding at areas undergoing high contact stress. The relative movements of mating surface can also cause galling, a form of high temperature wear. Several surface coating technologies have been developed to meet the stringent requirements of high performance, long life and service. Hard facing of stainless steels with nickel-base Colmonoy was adopted for various PFBR components to minimize induced radioactivity during maintenance, component handling and decommissioning. Colmonoy deposits would retain adequate hardness and to avoid dilution from austenitic SS substrate that may reduce deposit hardness, deposition was done by plasma transferred arc welding (PTAW) instead of conventional gas tungsten arc welding (GTAW) (Raj *et al*., 2008).

This procedure is successfully implemented for hard facing of roller bearings of the transfer arm, and the grid plate sleeves of PFBR. Wear-resistant bushes for transfer arm gripper assembly were fabricated by a novel procedure involving weld deposition of hard facing alloy on austenitic SS alloy by TIG welding procedure followed by precision machining of hard face deposits. Chromium nitride coatings with excellent thermal stability, wear and corrosion resistance has been developed for hard facing of grid plate sleeve components for enhanced resistance against galling of contacting surfaces, fretting and corrosion. The chromium is electroplated and the surface was modified by plasma nitriding to overcome disadvantages such as micro-cracks developed during electroplating. The Cr_2N formed was found to have a superior abrasive wear property. Alumina (Al_2O_3) coatings of 300 nm thick were obtained on oxygen-free high conductivity (OFHC) copper, stainless steel and mild steel substrates for sodium pump component applications using air plasma spray equipment. To overcome the disadvantage of the porosity of the coatings, a laser surface modification procedure (Raj *et al*., 2008) was adopted using multibeam CO_2 laser (Fig. 8).

Thus, by combining two powerful surface engineering techniques, plasma spraying and laser surface engineering, thick (>100µm) stable α-Al_2O_3 coatings over metallic substrates were obtained.

The reprocessing plants are designed with the objective of zero incident failures as leakages of pipes, vessels and equipment can considerably delay re-starting of operation and closure of plant. Fast reactor fuels are normally reprocessed by conventional PUREX process and coatings and surface modification have been attempted for enhancing the performance and service life of components made of Type 304L SS and titanium (Raj *et al*., 2006).

In nuclear fuel reprocessing, through aqueous route, Type 304 SS undergoes inter-granular corrosion due to inter-granular precipitation of chromium rich carbides in the temperature range of 773-1073 K. A new laser surface melting technique was developed (Kaul *et al*., 2009) to reduce sensitization of heat-affected zone of GTAW-welded 304 SS. The reason for enhanced IGC resistance is the significant increase in the fraction of $\Sigma 1$ boundaries, mostly subgrain boundaries. This is introduced by melting and resolidification. There are many disruptions in the grain boundary network by the intersecting subgrain boundaries that provide the IGC resistance.

Anodization was adopted to increase the corrosion resistance of titanium in both welded and wrought conditions. By the process termed as 'double oxide coating on titanium for reconditioning' (DOCTOR) three-fold reduction in corrosion rate of Ti was achieved. Mixed oxide coated titanium anodes MOCTAG developed for application as electrodes in reprocessing plants showed longer life compared to conventional MOCTA electrodes (Mudali *et al*., 2003). Nanostructured Ti, TiO_2, and ZrN coatings deposited on type 304L stainless steel (SS) by magnetron sputtering technique and Zr-based bulk metallic $Zr_{59}Ti_3Cu_{20}Al_{10}Ni_8$ alloy deposited on type 304L SS by pulsed laser deposition (PLD) technique showed improved corrosion resistance in nitric acid (Mudali *et al*., 2011).

In sodium-cooled fast reactor with metallic fuel, preference is for pyrochemical reprocessing route involving electro refining process, where the

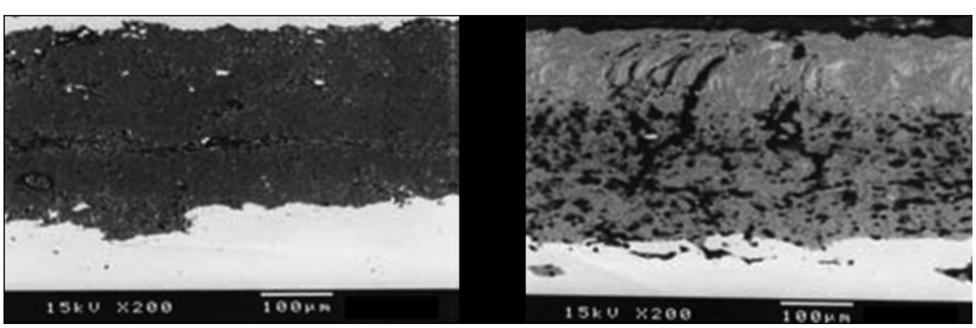

Fig. 8: Cross-sectional SEM micrograph of (a) as sprayed and (b) laser-treated alumina coating. Source: Raj *et al*. (2008)

electrolyte is molten chloride salt (LiCl-KCl) operating at 773 K. The electrorefiner is exposed to highly corrosive environments such as impure salts and high temperature. Efforts are on to select corrosion-resistant materials and protective coating technology for various operations such as salt preparation, electro refining and cathode processing. Various materials such as 410 SS, 430 SS, 316L SS and Inconel 600, 625 are being tested. Pyrolytic graphite and thermal barrier zirconia coatings were proposed to protect the equipment from aggressive chloride environment (Mudali *et al*., 2011). Yttria-stabilized zirconia coatings of 300 µm applied on type 316L SS with a metallic bond coating of 50 µm by an optimized plasma spray process rendered good corrosion resistance and laser melting of this coated surface provided additional benefits of defect-free surface (Shankar *et al*., 2007).

Graphite is also used for fabrication of electrodes, salt purification vessel liners and cathode processor crucible in pyrochemical processing. However, graphite degrades in molten salt and reacts with molten uranium. Cathode processor conditions were simulated by induction heat melting of uranium in yttria-stabilized zirconia and yttria-coated crucible and post-exposure characterization revealed that the coating offered better stability, ease of ingot release and coating adhesion (Shankar *et al*., 2010). Pyrolytic graphite deposited on graphite substrates by chemical vapour deposition using methane gas and tested in molten salt at 873 K for 2000 h in controlled argon atmosphere showed excellent corrosion resistance (Jagadeesh *et al*., 2013).

Role of Modelling in Development of Nuclear Materials

Presently, lifetimes are computed on basis of lab-based experimental data, constitutive laws, design rules and finally the available standards or codes. The empirical approaches and extrapolations are reaching their limits, and it becomes necessary to develop predictive tools to estimate materials behaviour for new materials and environments.

For radiation damage prediction, *multi-scale modeling* (Samaras *et al*., 2009) is pursued to examine if “seamless” joining of various concepts at various length and time scale can finally achieve an accurate prediction of lifetime of materials. This strategy combines *ab initio* calculations, molecular dynamics, Monte Carlo Method, the rate theory, dislocation dynamics, finite element methods and the continuum models. Combining the computation procedures with appropriate experimental validation would result in robust materials research.

As an example, for improving embrittlement in ferritics**,** grain boundary engineering was adopted. A number of modelling methods such as the Monte Carlo method, percolation model and fractal analysis have been carried out with the support of results from electron back-scattered diffraction (Karthikeyan *et al*., 2009). Size reduction of grains by 50% and DBTT reduction by 20°C could be achieved. High fractal dimension and fracture energy confirmed that the advantage was gained due to larger number of crack deflections or a tortuous path for the crack along its propagation route.

The finite difference method, Thermo-Calc, and DICTRA have been used (Anand *et al*., 2009) to study the mass transfer across dissimilar materials. The basic understanding of the process was based on molecular dynamics calculations which showed that sluggish diffusion of carbon in nickel compared to iron is responsible for prevention of formation of hard zone.

For predicting microstructures including the presence of delta ferrite, application of artificial neural network method successfully provided information to choose composition (Vasudevan *et al*., 2009) of filler metal required for joining stainless steel materials. Modelling for neutron-induced damage functions, corrosion predictions, microstructure stability, fracture mitigation, etc. are ongoing pursuits with unsolved challenges. Demands for new materials and performance conditions have inspired researchers and funding organizations to pursue new fascinating pursuits.

Ageing Assessment of Power Plants

Periodic health assessment and ageing management is an integral part of nuclear power technology to ensure safety and reliability in all phases of nuclear power, encompassing design, construction, commissioning, operation and waste management. Periodic monitoring will provide an early warning of any degradation in the components, equipment and systems of plants. Accurate technique for assessing the condition of components is the need of the hour. Special remote tools to inspect inaccessible core areas with high radiation fields and carrying out repairs are the biggest challenge to be met. NPCIL, BARC and other DAE institutes have developed many tools such as BARC Reactor Coolant inspection systems (BARCIS), Non-Intrusive vibration diagnostic technique (NIDVT), and specialized cameras, manipulators, welding tools, etc. which helped in pinpointing the exact locations, in determining the nature of repairs needed and in carrying out necessary repairs (Jain *et al*., 2010). In Indian PHWRs, health assessment during operation using techniques developed in-house revealed life limitation of Zr-2 coolant channels due to degradation of properties on exposure to intense radiation, high temperature and pressure in a corrosive environment. Experiences in India and worldwide have led to the coolant tubes of Zircaloy-2 being replaced by Zirconium – 2.5% Niobium, a better material by carrying out success enmasse coolant channel replacement (EMCCR) using indigenous technology. The time, cost and manrem (radiation dose) levels in EMCCR have been progressively reduced through innovations in tooling and job execution. Flow-assisted corrosion (FAC) of carbon steel feeder tubes in Indian PHWRs was lower by maintaining the pH of primary coolant in a narrow band of 10.2 to 10.4. However, life was extended by replacing the same with a better carbon steel material with 0.2% chromium content which has more resistance to FAC by en-masse feeder replacement (EMFR). The detection and correction of leaky steam generator tubes helped in preventing leakage of expensive and radioactive heavy water coolant and the contamination of secondary system. Also, the Monel-400 SG tubes were replaced later by Incoloy-800.

Various NDT techniques are employed for monitoring and avoiding failures, life assessment and extension of components of nuclear power plants (Raj *et al*., 1997). Periodic monitoring of heat exchanger tubes is done by eddy current testing technique and to eliminate signals from unwanted parameters such as baffle plate multi frequency technique was adopted. For pre-service and in-service inspection of ferromagnetic tubes, remote Field Eddy Current Testing with higher sensitivity was adopted. Eddy current imaging technique can detect defects such as fatigue cracks, corrosion pits and electrical discharge machining (EDM) notches. Ultrasonic thickness gauges can detect exfoliation, stress corrosion cracking and material thinning by scattering of ultrasound and is detected by shear waves in an angular incidence. Ultrasonic phased array probe systems have capabilities to detect flaws even in complex geometries of pipes, elbows and nozzles. To inspect tube conditions inside the tube sheet, a technique called quantitative ultrasonic analysis system and recorder (QUASAR) or internal rotary inspection system (IRIS) has been utilized with success. FLEXIMAT is an innovative method, which uses 12 or more ultrasonic array elements on a flexible, printed strip connected to a flaw detector for continuous monitoring of corrosion/erosion in vessels, pipelines, pipe bends, etc. Radiography testing techniques have proven to be more effective for a range of components including pipes of 0.2 m OD and a wall thickness of 0.018 m using field gamma ray source of Ir-192 and Co-60 of 1000 Ci strength. Acoustic emission technique (AET) has been successfully applied for detection and location of leak paths present on an inaccessible side of an end shield of Rajasthan Atomic Power Station 1. Frequency spectral analysis approach was used and the difference in the characteristic frequency of the signal for two leak paths detected was attributed to the size, shape and morphology of the leak path. In a condition assessment campaign, two possible leaking pressure tubes among 306 pressure tubes in MAPS 1 were detected (Raj *et al*., 1997) using AET technique where ratio of the spectral energy between two different frequency bands, namely 700 to 1000 kHz and 40 to 175 kHz and its variation with an increase in pressure helped to narrow down the suspect channels to two numbers.

For assessment of internals of pipes and tubes, a technique called laser optic tubing inspection system (LOTIS) has possibilities of reducing time for in-service inspection. In the system, a 40 micron diameter laser beam is projected at near-normal incidence onto the tube inner surface using accurate rotational drive system and receiving optics image this spot of light into a single axis lateral effect photo detector. Intelligent pigs based on magnetic flux leakage (MFL), ultrasonics and high frequency eddy current are used for inspecting pipelines for corrosion defects. Ultrasonic pigs provide a good quantification of defect size. High frequency eddy current pigs due to its accuracy and reproducibility is used in successive inspections to determine corrosion rates of small diameter heavy-walled pipelines.

A three-level approach for life assessment has been evolved (Viswanathan *et al*., 1997) for life extension of nuclear plant components which undergo cracking failure. Simple calculation techniques in the first level are followed by non-destructive and destructive techniques, respectively in the next two levels. Development was achieved in five select areas of technology; the life fraction rule, creep cavitations, evaluation of weldments, high temperature crack growth and estimation of toughness. Life fraction rule for creep states that while calculating cumulative damage under changing operating conditions, the ductility of the material needs to be considered. For brittle materials that are prone to Type IV cavitations, fusion line cavitations, etc., temperature accelerated tests may cause premature failure and isostress extrapolation of the accelerated test results may lead to conservative prediction of remaining life at the operating temperature. The actual remaining life under operating conditions may well exceed the estimation from accelerated tests. Attempts for quantitative correlations of cavitation with remaining life are being made on basis of interrupted-creep tests (Ellis *et al*., 1989) on simulated heat-affected zones of materials. However, results showed that scatter was too much to verify the life-prediction model of Cane (Cainsand Shammas, 1984); and hence damage classification has been correlated with life fraction; and for each-class of material, a life-fraction range established. This data is utilized for setting inspection intervals.

The determination of critical crack-size based on knowledge of the current toughness of the material at the critical location is a crucial last step in remaining-life analysis of cracked components. By non-destructive estimation of 50% ductile to brittle fracture appearance, transition temperature and correlating with K_{IC}, the critical crack size for failure is determined. By conducting tests at different temperatures using a small punch specimen, a curve of adsorbed energy versus temperature can be developed and midpoint was used to define ductile to brittle transition temperatures (Cainsand Shammas, 1984).

Material Challenges in Future Fission Reactors: Generation IV Perspectives

The ever increasing demand on nuclear materials is graphically represented in Fig. 9 (Zinkle and Busby, 2009). The ability to withstand increasing operating temperature, stress levels, irradiation dosages and corrosive environments, fabrication capabilities, compatibility with envisaged reprocessing schedules at the backend of fuel cycle, availability at reasonable costs and industrial friendly materials technologies are the aspirations.

Newer structural materials have to be developed that can operate at higher temperatures than the present limit set by Gen III reactor concepts that include both thermal (LWR and PHWR), fast reactor (MOX and metal-fuelled) and advanced high temperature hybrid reactor. Fig. 10 shows a schematic

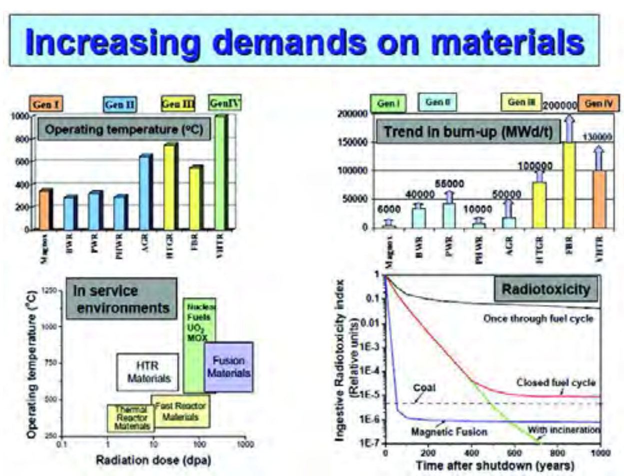

Fig. 9: Graphical summary of the increasing demand placed on nuclear materials. Source: Zinkle and Busby (2009)

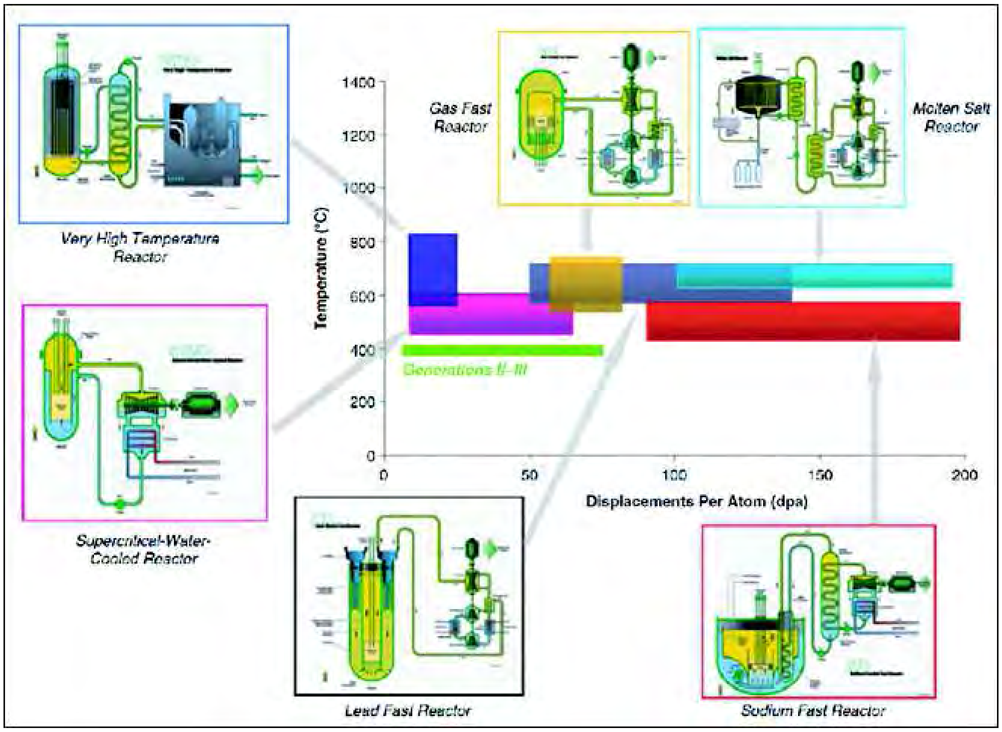

Fig. 10: Schematic collage of advanced reactor concepts. Source: Zinkleand Busby (2009)

of certain advanced reactor concepts known as "Generation IV" (Zinkle and Busby, 2009). These reactor designs for producing clean and economical nuclear energy aim at maximizing the fuel burn-up and operating thermal efficiency. Thus, the design operating temperatures are high calling for development of innovative materials. These materials also need to face extended burn-up, and should possess double the resistance for neutron and high energy gamma radiation. For better heat removal, the coolants adopted in the high temperature designs are Pb-Bi alloy. The structural materials including liquid metal pumping motors should be compatible with this more corrosive environment.

The Gen IV reactor systems aim at sustainability criteria with enhanced safety, proliferation resistance and cost competitiveness. Emphasis is laid on closed fuel cycle philosophy. Design and development of low swelling, creep resistant, acceptable corrosion mitigation, reduced activation variants of established structural materials is central to realizing advanced Gen IV reactors. Tables 5 and 6 summarize the basic characteristics of different advanced reactor types (Gen IV) and materials (Zinkle and Was, 2013).

Structural materials used in the cores of advanced reactors face high operating temperature and simultaneous presence of intense knock-on displacement damage by the fission neutrons. As per Table 5, SFR, LFR and MSR have high temperature, high-dose operating environment that place increasing emphasis on strength, creep, creep-fatigue and fracture toughness at low temperatures for the materials used. Though TiC precipitates in Ti-modified austenitic steels, it has swelling-resistant microstructure that helps to extend low-swelling transient regime. These alloys are not sufficient to avoid significant void swelling in the operating conditions of Gen IV. More radiation-resistant alloys such as 2.5-12% Cr bainitic-ferritic-martensitic steels are considered for high dose core internal and reactor pressure vessel applications (Zinkle and Was, 2013). Controlled additions of Ti and P to austenitic Fe-Cr-Ni alloys are shown to produce fine dispersions of TiC or M_2P (M=Fe etc.) precipitates that provide dramatic void swelling resistance after ~100 dpa irradiation compared to standard Fe-Cr-Ni alloys (Lee *et al*., 1990). Nanometer-sized Y, Ti, O-rich particles in oxide-dispersion-strengthened alloys, in current

Table 5 & 6: Advanced fission reactor core environments

System	Coolant	Pressure (MPa)	T_{in}/T_{out} (°C)	Neutron spectrum maximum dose (dpa)
Supercritical water cooled reactor SCWR	Supercritical water	25	290/600	Thermal ~30, Fast ~70
Very high temperature reactor VHTR	Helium	7	600/1000	Thermal <20
Gas Fast Reactor GFR	Helium supercritical CO_2	7	450/850	Fast, 80
Sodium Fast Reactor SFR	Sodium	0.1	370/550	Fast, 200
Lead fast reactor LFR	Lead or Lead-Bismuth	0.1	600/800	Fast, 150
Molten salt reactor MSR	Molten salt FLiNaK	0.1	700/1000	Thermal, 200

System	Fuel	Cladding	In-core structural materials	Out-of-core structural materials
Supercritical water cooled reactor SCWR	UO_2	F-M (12Cr, 9Cr) (Fe-35Ni-25Cr-0.3Ti), Incoloy, ODS, Inconel 690, 625, 718	Same as cladding plus low swelling stainless steel	Ferritic martensitic low alloy steel
Very high temperature reactor VHTR	UO_2, UCO	SiC or ZrC coating and surrounding graphite	Graphites, PyC, SiC, ZrC Vessel: F-M	Ni-based superalloys, 32Ni-25Cr-20Fe-12.5 W-0.05C,Ni-23Cr-18 W-0.2C, F-M w/thermal barriers, low-alloy steels
Gas Fast Reactor GFR	Mixed carbide (U,Pu) C	Ceramic	Refractory metals and alloys, ceramics, ODS, Vessel: F-M	Ni-based superalloys, 32Ni-25Cr-20Fe-12.5 W-0.05C,Ni-23Cr-18 W-0.2C, F-M w/thermal barriers, low-alloy steels
Sodium Fast Reactor SFR	MOX or U-Pu-Zr or MC or MN	F-M or F-M ODS	F-M ducts, 316SS grid plate	Ferritics, Austenitics
Lead fast reactor LFR	Mixed nitride (U,Pu)N	High Si F-M, ODS, ceramics, refractory alloys	High-Si,F-M, ODS	High-Si austenitic Ceramics or refractory alloys
Molten salt reactor MSR	Salt	Not applicable	Ceramics, refractory metals, high-Mo Ni-based alloy (INOR-8) graphite Hastelloy-N	High-Mo Ni-based alloys (INOR-8)

Source: Zinkle and Was (2013)

studies, assure good stability under irradiation and significant strength advantages over ferritic-martensitic alloys for high temperatures upto 923K.

In very high temperature gas-cooled reactors such as gas-cooled GFR or VHTR, where materials must withstand temperatures approaching 1000°C, due to rapid kinetics of corrosion and oxidation, specially manufactured "nuclear" grade graphite and ceramic composites are proposed as candidates for structural materials. For the intermediate heat exchanger where high-temperature helium gas is present, nickel based alloys such as Inconel 617 and Haynes 230 are used. Oxidation, decarburization and carburization can occur at the surface of heat exchangers and development of protective coatings without compromising thermal conductivity is the most important challenge to structural materials in VHTR.

For SCWR, the only water-cooled reactor among the Gen IV design, very high pressure to maintain water in the supercritical state is needed. The major challenge for materials in the SCW environment is the resistance to SCC and irradiation-assisted SCC. Austenitic stainless steels and nickel based alloys suffered IGSCC in deaerated SCW at 400°C (Allen *et al*., 2012) and ferritic-martensitic steels showed SCC resistance in the same temperature range (Ampornrat *et al*., 2009). Austenitic stainless steels exhibited extreme embrittlement under neutron irradiation of 40 dpa in SCW; however, ferritic-martensitic steels showed good resistance (Teysseyre *et al*., 2007).

Conclusions

Nuclear energy shall remain a firm option for large-scale energy production by many countries in the world. The nuclear industry is forging ahead with advanced technologies to achieve safe, economic, proliferation-resistant nuclear reactors with minimum nuclear waste. Ever since the genesis of nuclear energy, development of materials and relevant technologies was considered as a challenging task. From Zircaloy to Zr-Nb alloys, from aluminum alloys to austenitic stainless steels and ferritic steels to oxide dispersion strengthened steels, nuclear reactor environments demand a wide spectrum of materials with high performance. State-of-the-art development in the field of materials science and technology can meet targets such as increased burn-up of fuel and enhanced lifetime of reactors. However, substantial R&D on high-temperature irradiation and creep resistant alloys, composites and ceramics for fuel rod cladding, ODS alloys with robust manufacturing process, low-activation steels, high performance coatings and the related processing technologies is essential to meet the demands of advanced nuclear technologies. With greater understanding of irradiation-assisted degradation mechanisms, a bottom-up design approach has to be evolved where controlling composition, morphology and interface-defect interaction enable us to perform atomic-scale design of extremely radiation-tolerant materials. The key direction is to replace past empiricism appropriately with accurate knowledge-based design. Exciting challenges and opportunities await materials technologists and successful response will pave the way for the society to enjoy sustainable pollution-free energy in future.

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