# Structural Materials for Nuclear Industry

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**Preamble**

Since its inception, DAE has given special attention on the development of materials for nuclear applications and beyond. These special efforts culminated into the development of a host of materials up to their commercial usage. This chapter provides a glimpse of the all-around development of materials including the journey of few of the materials from ore to the finished products. Special efforts made in the Materials Group, BARC to assess the performance of the materials, modifications introduced to improve their performances and development of special materials to cater to the specific needs in nuclear industry are briefly presented.

## 1. Bhabha's Vision

Nuclear installations, be it reactors, heavy water plants or waste immobilization facilities, use a variety of materials out of which some are load bearing or structural materials. It is very difficult to procure these materials from abroad because of the many restrictions on nuclear installations of the country. The founder of our nuclear programme, Dr. Homi Bhabha had exemplary foresight and had foreseen the hurdles, the country would be encountering in taking its nuclear energy programmes ahead. He started taking steps for achieving self-reliance in all aspects of our nuclear energy programme, right from the beginning. A different department was created to first start exploring the presence of elements useful for nuclear energy programme in the earth crust of the country. This required scientists with good geological knowledge. Once a promising deposit was located, it needs to be mined and processed. The mined material needs to be subjected to mineral dressing and the knowledge of how to convert the concentrated ore into metal. So, there was a need for creating an indigenous knowledge bank of mineral exploration, mining, ore dressing, chemistry and thermodynamics and different aspects of metallurgy. In order to create a research base on the aforementioned subjects, research centres were setup. Atomic Minerals Directorate was setup for exploration, mining and to do research on some aspects of mineral dressing. Bhabha Atomic Research Centre (BARC) had scientists working on mineral dressing and extractive metallurgy. The scientists of this centre carried out extensive research on extraction of metals from Indian resources. The knowledge bank so created was helpful in developing flow sheets for metal extraction from Indian ores. Since, the Indian ores are different from those from other countries in many cases, the technology developed was India specific. Based on these technologies, Uranium Corporation of India was set up for making uranium oxide and Nuclear Fuel Complex was set up for making Zr and the Zr based alloys.

Once the element or metal is produced, it needs to be mixed with other elements to make a suitable alloy or a compound catering to the need of the applications. Here, a detailed knowledge of alloying and alloy design aspects are needed. The metal produced is transferred to a melting facility where an ingot is produced. The ingot produced is subjected to various thermo-mechanical operations like forging or extrusion to break the cast structure. Here, knowledge about physical metallurgy of the alloy is needed and so is the knowledge about mechanical metallurgy which essentially focuses on the hot and cold deformation behaviour. The broken cast structure is further subjected to the different rolling or extrusion operations to give it a desired shape. The knowledge of the effect of deformation and heat treatment not only on the microstructure but also the crystallographic alignments of grains representing texture is very important so the alloy not only gets a useful shape and has the desired microstructure but also texture. Once a product is made, it needs to undergo various quality checks to ascertain to its defect free nature. It may also be tested for its mechanical properties, corrosion behaviour and in some cases irradiation tolerance. Since the irradiation tolerance against neutrons is rather difficult to evaluate outside a nuclear reactor, proxy ion irradiation is used in the Variable Energy Cyclotron Centre (VECC).

As can be seen from the aforementioned description of sequences of steps required for manufacturing a product from Indian raw materials, involvement of many agenises is required. Accordingly, Bhabha's long standing vision led to the creation of all these agencies and an infrastructure for making almost all structural materials needed for the Indian nuclear energy programme from Indian resources.

## 2. Structural Materials for Nuclear Reactors: An Introduction

The keystone for the development of nuclear structural materials is the containment of nuclear fuel and radiation generated fission products during normal as well as abnormal reactor operating conditions. Therefore, reliable performance of structural materials is the most important criterion for the successful operation of a nuclear reactor. These structural materials are subjected to high-energy neutrons, corrosive environment along with intense mechanical and thermal stresses during their use in the reactor. The performance of a nuclear reactor can be improved by selecting suitable structural materials which offer higher margins for safety and better flexibility in the material design, in particular, by offering higher strength, better thermal creep resistance and superior corrosion properties and higher tolerance to neutron radiation damage. In nuclear industry, structural materials require special attention in terms of their compositions and microstructures, as any minor unwanted alteration may affect the life span of the material in the reactor. For example, zirconium-based alloy components which form the major part of the in-core structural material are processed in different manner for each component to achieve the most suitable combination of their properties required for the application. Attaining such microstructures which offer most optimum properties in these alloys through proper selection of the processing parameters is a major challenge for metallurgists. This aspect also draws considerable attention in the processing of these material. In general, strategy for designing high-performance materials takes several factors into account. Considerable research has gone in the development of these nuclear materials.

### *2.1. Zirconium based alloys:*

Among all the structural materials used in various reactors, Zr based alloys like zircaloy-2, zircaloy-4 and Zr-2.5%Nb, are the most prominent material currently being used for reactor core structural applications. However, their anisotropic properties, composition and the methods of fabrication need special attention. By tailoring microstructure and texture of zirconium-based alloys based on specific requirements suitable properties can be induced in the structural component. Such optimization in the microstructure can be achieved by the selection of complex thermo-mechanical processing during the fabrication of the structural components for nuclear reactors. Microstructure developed through these process determines the long and short term properties of the components. In addition, these alloys have shown variety of phase transformations. Due to amenability to these phase transformations-involving both diffusion-less and diffusional transformation-a variety of microstructures can be produced in Zr based alloys.

### *2.2. Steels*

Steels are another structural material which are used on a large tonnage basis in nuclear industry. Plain carbon steels are used as piping and components in the secondary circuit of nuclear power plants (NPPs). Such plain carbon steels are highly prone to flow accelerated corrosion (FAC) and an extensive pipeline thinning management program has been put in place in Indian NPPs to avoid unexpected failures.

Stainless steels (SS), austenitic, ferritic and martensitic varieties, are used in different components in NPPs, nuclear spent fuel reprocessing and waste management plants and various other plants in nuclear industry. Materials Group, BARC has been working on all the varieties of stainless steels used in NPPs and has made significant contributions in improving the corrosion resistance of SSs and establishing degradation modes in operating plants. While sensitization, intergranular corrosion (IGC), intergranular stress corrosion cracking (IGSCC) are the most prominent issues, newer concepts of grain boundary engineering and development of the understanding of IGC of even solution annealed stainless steels in highly oxidizing nitric acid conditions (near transpassive potential regime) have been developed. Role of addition of nitrogen to type 304L stainless steel in improving IGSCC resistance, detailed understanding of the susceptibility of martensitic SS e.g., type 420 SS are some examples of the novel approaches used to improve the performance of these structural materials in the nuclear industry. Recently developed, *R*educed *A*ctivation *F*erritic-*M*artensitic (RAFM) steels is an example of the development of a steel for specific applications in nuclear industry. Maraging steels are another important category of steels that rely on alloying additions and microstructural control to obtain high strength, hardness and flowability/fabricability. In-depth understanding of the mechanisms of strengthening in maraging steel has been developed in BARC.

### *2.3. Nickel Based Alloys*

Another alloy system, which is commonly used in nuclear industry, are nickel-based alloys. Mostly, these alloys are used as steam generators (SG) tubes in NPPs. Hence, the importance to keep the corrosion damage as well as the corrosion rates to a minimum is of primary importance. The currently preferred SG tubing materials for NPPs are alloy 690 and alloy 800. Although many reactors are still in operation with alloy 600 as the tubing material,but this alloy has experienced many corrosion-related problems and is being replaced by alloy 690. It may be noted thatalloy 600 and alloy 690 are categorized under Ni-Cr-Fe alloys whereas Alloy 800 as a non-ferrous alloy. Other Ni based alloys are also, in general, used for high temperature applications e.g., reformer tubes in Heavy Water Plants. In addition, Ni based alloys are also being developed as a structural material for Gen IV nuclear reactors. Development of Ni-Mo-Cr alloys for high temperature Gen IV reactors is an ongoing research activity.

## 3. Pioneers in Materials Development:

In the program on the development of Materials for nuclear reactors, many scientists, Dr. Brahm Prakash, Dr. C. V. Sundaram, Dr. P. R. Roy, Dr. C. K. Gupta have made pioneering contributions in the extraction, processing and scaling upto the commercial production for many metals and its alloys (Fig.1).While Dr. Brahm Prakash was instrumental in the establishment of commercial unit like Nuclear Fuel complex, Dr. Sundaram and colleagues developed the solvent extraction process for separating Zr and Hf as well as process flowsheets for refractory metals like Nb and Ta. Among these, Dr.Srikumar Banerjee was a pioneer metallurgist who devoted his life-time in understanding phase transformation in Zr, Tiand Ni based alloys and tailoring microstructure/grain boundary engineering to obtain optimum performance from steels and stainless steels. His basic approach to first generate an understanding of the material and its microstructure and then correlating it to the properties of these structural materials was a key element in the success of materials development.

**Fig.1: Brahm Prakash showing the fabrication and testing of the indigenously produced Zr based tubes to Shri Lal Bahadur Shastri, then Prime Minister of India**

## 4. Materials Requirements for Nuclear Reactors

Currently two types of water-cooled nuclear power reactors are under operation. In the first type, the entire core of a reactor is enclosed in a large steel pressure vessel filled with ordinary water. The water acts as a heat transfer medium and neutron moderator. Such reactors, commonly known as pressurised water reactor (PWR) and boiling water reactor (BWR). In these reactors zirconium-based alloys are used for the cladding tubes which encapsulate the uranium dioxide fuel pellets. The reactor operating at Tarapur near Bombay is an exampleof the BWR reactor and the reactor operating at Kudankulam is an example of PWR.

In the second type reactors, the pressure vessels are replaced by a large number of pressure tubes through which heavy water flows under high pressure to extract heat from individual fuel elements. These pressure tubes pass through a calandria vessel containing cool, heavy water as moderator. Each pressure tube is separated from the surrounding by a calandria tube and an insulating gas is provided to separate hot pressure tubefrom ambient temperature the moderator water. Operating reactors of this type are commonly known as the pressurised heavy water-cooled reactors (PHWR). PHWRs are the back bone of Indian nuclear program on electricity generation. In PHWR, the fuel-cladding tubes, the pressure tubes and calandria tubes are all made of Zr- alloys. Among these tubes, fuel tubes are thin-walled tubes (0.4 to 0.8 mm) which undergo complex sequence of bi-axial and tri-axial tensile stresses, creep and recovery strains during their typical operating life time of 30,000 hours. The pressure tubes in PHWR, on the other hand, are six-meter-long tubes with the minimum of 3.5 mm wall thickness. Unlike the fuel-cladding tubes which are timely replaced by a fresh lot, pressure tubes remain inside the reactor nearly to the life-time of a reactor. Therefore, a typical pressure tube must maintain its very high integrity throughout a life span exceeding 200,000 hour. Although, small cracks and even failure of a tube can be tolerated and faulty tubes can be replaced intermittently, such an exercise is an expensive proposition and not a desirable condition. The calandria tubes typically have a wall thickness of ~1.25 mm and ~107 mm internal diameter. Generally, the conditions on calandria tubesare less severe than those prevail on fuel or pressure tubes. Based on inputs from the research and development on Zr alloys, its mechanical and corrosion behaviour, Nuclear Fuels Complex (NFC) produces various components of Zr based alloys for nuclear reactors, as shown in Fig. 2.

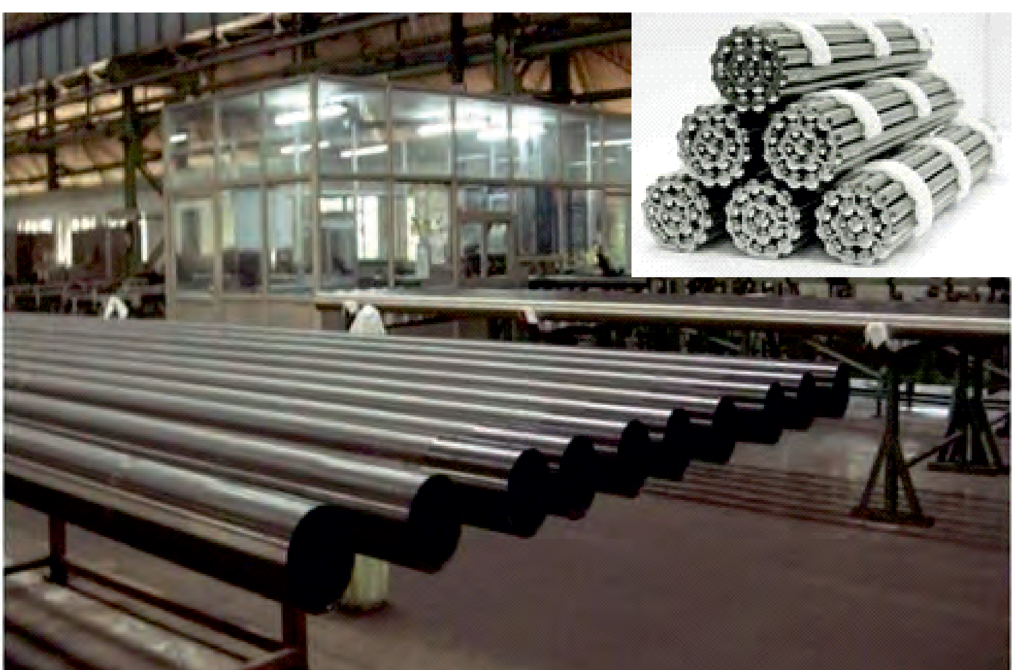


**Fig. 2: Photo of pressure tubes produced at NFC. Inset shows fuel bundles produced at NFC**

### *4.1. Zr Based Alloys*

The work on the development of metallurgy of zirconium based materials is essentially due to their applications as structural material in the nuclear industry. Zr based alloys show their unique combination of low capture cross-section for thermal neutrons and good corrosion resistance in high temperature water (~300°C) [1].

The principal source of zirconium is zircon (zirconium silicate ($ZrSiO_4$)) which is found in the coastal beach sand in India. This sand also contains many other valuable minerals because of which a special physical beneficiation technology for the separation of the individual minerals was first established at BARC, Trombay at a pilot plant scale and subsequently, a plant was established in Tamil Nadu by Indian Rare Earths Limited (IREL) for the processing of Manavalakurichi beach sand. The zircon contains about 2.5% Hf, an element chemically similar to Zr and it was successfully separated at BARC using vapour phase dechlorination technique. A process for separation of Zr and Hf was developed by chlorination of Zircon, purification to obtain $ZrCl_4$ and $HfCl_4$mixed salt, selective dichlorination of $ZrCl_4$ from the vapour phase. This led to the formation of pure $ZrO_2$ in the residue by adjusting the ratio of the flowing gas mixture composed of chlorine and oxygen at high temperatures leaving the volatiles enriched with $HfCl_4$. Solvent extraction process was developed later for a more effective and larger scale separation of the two elements. Chlorination of $ZrO_2$was further optimized using static-bed reactor technology. Magnesio-thermic reduction of $ZrCl_4$ producing pure zirconium, Kroll process, was used for making zirconium sponge at BARC, Trombay and a schematic of the initially designed assembly having different heating zones used for carrying out Kroll process is shown in Fig. 3a [2].Iodide refining technology (Van Arkel-De Boer Process) was developed and demonstrated by C. V. Sundaram and his colleagues at BARC for making ultra-pure zirconium from impure zirconium and zirconium alloy scraps [2]. Fig. 3b shows anoutlook of the zirconium crystal grown by iodide refining process, and the inset of the figure represents the overall view of the crystal bar zirconium formed on U-shaped zirconium filament. Zirconium produced by Kroll process was subsequently vacuum arc melted to produce various zirconium alloys, such as Zircaloy 2, Zircaloy 4, Zr-2.5Nb, Zr-2.5Nb-0.5Cu, for structural components in nuclear reactors. A dedicated plant was further established in 1971 for the production of Zr and its alloys, and for the fabrication of different reactor components at NFC, Hyderabad.

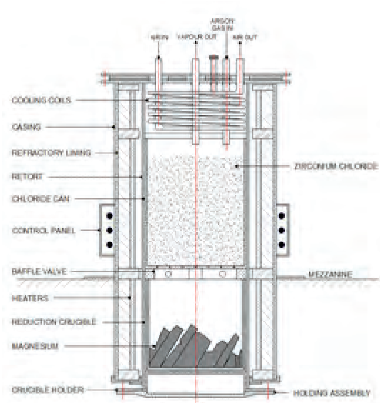



**Fig. 3a: Schematic of the Kroll reduction assembly for zirconium sponge production designed at Bhabha Atomic Research Centre, Trombay**

**Fig. 3b: Zirconium crystal bar grown by iodide refining technique at BARC campus and the inset shows the crystal bar zirconium formed on U-shaped zirconium filament**

In the early stage of development of zirconium-based technology, emphasis was given on the purity of zirconium as the raw material. However, very soon it was realized that very high purity of the product was not necessary. In fact, very soon it was realized that purer material has lower corrosion resistance in comparison to the impure materials. It was attributed to the presence of impurity elements like Ni, Cr or Fe, which were helpful in improving the corrosion resistance to Zr.

The first stage of the development program of Zr-alloys was to identify elements which can improve the corrosion resistance of Zr. First set of elements which were identified in decreasing order of effectiveness are tin, tantalum and niobium. Tin was selected as it was most effective in improving corrosion resistance without seriously affecting the neutron economy. The first series of Zircaloys was nearly binary alloy with nominal composition as Zr-2.5%Sn. This alloy was named as 'Zircaloy-1'. Zircaloy-1, when subjected to long-term high temperature water corrosion testing, gave disturbing trends. In place of expected decreasing rate of corrosion, the corrosion rates after a transition time increased and remained constant thereafter. Thus, an urgent search for an alternative alloy was initiated. Desperate attempts led to an accidental discovery of an alloy which, in fact, was the contamination of Zircaloy-1 with stainless steel. The resultant material proved to have substantially improved corrosion resistance. Subsequently the optimized alloy composition was worked out in terms of the iron content which was nominally set at 0.15%, nickel 0.05% because of its beneficial effect on high temperature corrosion resistance, 0.1% chromiumwas picked up as an impurity from the stainless-steel reacting vessels and Sn was reduce to 1.5 %, which was found to be adequate to mitigate the deleterious effects of nitrogen. This new alloy composition was designated as 'Zircaloy-2'. Zircaloy-2 was the structural material used for all nuclear reactors of that generation.

It was assumed that with increasing time Zircaloy-2 would also show accelerated corrosion similar to Zircaloy 1. A new alloy was therefore proposed where Sn was reduced to 0.25% and addition of 0.25% Fe was maintained to increase the strength of the alloy. This new alloy was designated as Zircaloy-3. During corrosion testing, this alloy could not outperform Zircaloy-2 and its inferior mechanical properties in comparison to Zircaloy-2 led to the discontinuation of the work on the alloy. During this time, deleterious effects of hydrogen on the strength of Zr component used in the core of a nuclear reactor was realized. A correlation between the hydrogen concentration and impact toughness led to intense research on the understanding of hydrogen behaviour in Zr alloys. In one such set of experiments, coating of nickel on Zircaloy plates showed significant increase in hydrogen pick-up. This observation led to the removal of Ni in the composition of Zircaloy-2 and the new alloys was called as “Ni-free Zircaloy-2”. However, this new alloy was having poor corrosion resistance. In later alloy when the loss of the Ni was compensated with increase in Fe, the alloy matched all the properties of Zircaloy-2 and with pick up of hydrogen nearly half of the Zircaloy-2. This new alloy was called “Zircaloy-4”

Currently, Zircaloy-2 and Zircaloy-4 are widely accepted Zircaloy-series of alloys for nuclear applications. However, hydrogen related problem became a daunting issue as the picked-up hydrogen during the operation of the reactor started precipitating in certain crystallographic direction during the cooling of reactors making the tubes susceptible for catastrophic failures. This led to the development of another alloy system with second best choice of element, niobium.

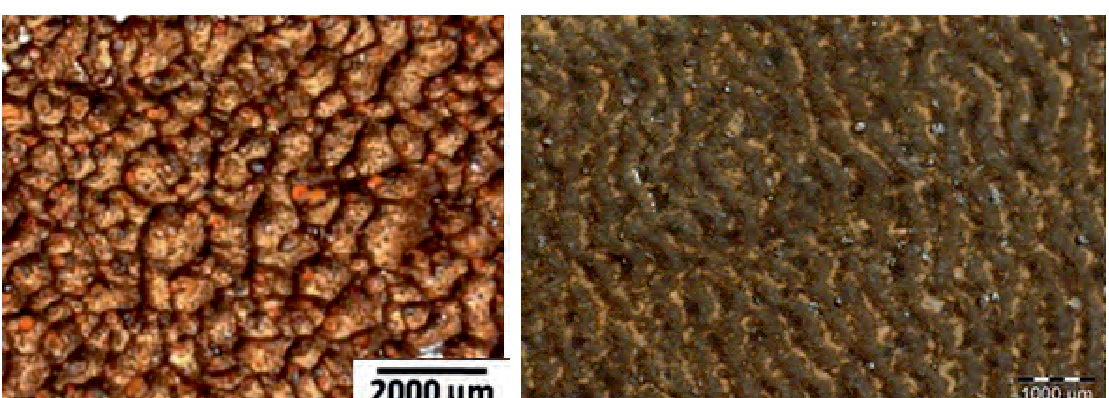
Initial development work on Zr-Nb alloy was carried out by Russian researchers. Among various alloys of Zr-Nb alloy systems, Zr-2.5Nb alloy was selected for pressure tube materials. The two-phase structure of the alloy offered much higher strength with adequate ductility. The presence of Nb in the alloy reduced the oxidation and hydrogen pick up in the pressure tubes. These qualities of Zr-2.5Nballoy allowed it to outperform Zircaloy-2 and, therefore, in later reactors Zr-2.5 Nb alloy replaced Zircaloy-2 as pressure tube materials.

Typical fabrication route for Zr-2.5 %Nb pressure tubes involves a combination of hot and room temperature working. The hot working is generally carried out in the (α+β) phase field where either forging or hot extrusion and involved. The room temperature work is in India is carried out using a pilgering route. This complex themo-mechanical treatment determines the volume fractions of the two phases, and their compositions, the aspect ratios of the α and β-grains and the crystallographic texture of the product. High strength along with a good ductility and toughness of Zr-2.5%Nb pressure tubes is essentially derived from the fine (α+β) fibrous microstructure consisting of elongated α-grains and the β phase stringers primarily located at α-grain boundaries. These microstructures are being constantly reproduced in nuclear fuel complex in components as large as 6 meters which could be considered as engineering marvels produced by Indian scientists and engineers [3].

### *4.2. Steels*

#### *4.2.1. Plain carbon steels*

AISI A333 Grade 6 and AISI A106 Grade Bare extensively used for various pipelines and other components in the secondary circuit of NPPs (PHWRs and PWRs). A generic degradation mode is flow assisted corrosion (FAC) – both single phase FAC and two-phase FAC. FAC is a corrosion mechanism in which normally protective oxide layer on a metal surface dissolves in a flowing water. The underlying metal corrodes to re-create the oxide, and thus, the loss of the metal continues. Based on an extensive program, BARC examined the inner diameter surfaces of the components affected by thinning and removed from service from all the NPPs in Indiaandlarge database was created correlating the scallop size to the FAC rate. This database is now used to predict the FAC rate at a given location of a component. Typical signature patterns of single and dual phase FAC have been captured from the affected components and used to independently establish the mode (single or two phase FAC or erosion) of degradation (Fig.4). After establishing FAC prone segments in secondary circuit and from the basic knowledge available on such degradation, changes in chemical composition specification have now been incorporated for the feeder piping in primary circuit to impart additional resistance to FAC [4,5].




(a) (b)

**Fig. 4:Typical signature pattern for (a) Single phase FAC (Scallops) and (b) Dual phase FAC (tiger stripe pattern) observed on Indian PHWRs secondary circuit components**

*4.2.2. Low alloy steels*

Low alloy steels involving alloying elements likeMn-Ni-Mo (commonly known as western grade steels) orCr-Mo-V steels (commonly known as eastern grade steels)are widely usedas the structural material for the fabrication of reactor pressure vessel (RPVs) due to theirhigh strength and toughness. Prolonged operation under reactor operating conditions (neutron flux and temperature) results in the degradation of properties. The major degradation in mechanical properties of the RPV steel during reactor operation is ascribed to irradiation induced embrittlement. Since, the life of a reactor depends on the integrity of the RPVs, understanding the microstructural developments that occur all along in-service and their effect on the performance is of paramount importance. A detailed study wascarried out on acceleratedthermal aging at 450 °C up to 8,400 h. These experiments showed that the thermal aging embrittlement of Mn-Ni-Mo steel is primarily due to phosphorous impurity segregation at the grain boundaries.

In the easterngrade steel,both impact toughness and hardness reduced monotonically with transgranular cleavage fracture region increasing of aging duration. In this steel though sign of impurity segregationwere absent, transformation of Cr-rich $M_7C_3$ to $M_{23}C_6$ (M= Fe, Cr & Mo) carbides along with its coarsening and the corresponding Cr-Mo depletion at the carbide-matrix interface region appear to be the main reasons responsible for thermal aging embrittlement in these steels.

In order to evaluate the properties of these steels a relatively new approach was adopted where in place of full-size sample, small punch testspecimens were (miniaturised mechanical testing; 10 mm × 10 mm × 5 mm) used, which enabled easy extraction of specimens from the components in service (including irradiated specimens). SP tests could clearly capture the embrittlement due to thermal aging for both the steelsas investigated by the conventional CVN testing.

*4.2.3. Stainless steels*

It is a well-known fact that stainless steels derive their stainless properties due to the presence of oxides of chromium at the grain boundaries. Any depletion of these oxides compromises the corrosion resistance of the steel. Therefore, special efforts were made in BARC to improve the properties of the steels. The key features of the work on stainless steels are

(a) Grain boundary engineering to improve resistance to sensitization, intergranular corrosion (IGC) and intergranular stress corrosion cracking (IGSCC),

(b) development of nitric acid grade (NAG) SS and its use in spent fuel reprocessing and waste management plants,

(c) developing understating of IGC of austenitic SSs in applications in nitric acid with high operating potential and alternate alloys suitable for such applications,

(d) mechanism of addition of nitrogen to type 304L SS in improving its resistance to IGSCC in reactor simulated operating conditions and the role of a higher nitrogen making it even more prone to IGSCC, even in an annealed condition (in a worked condition) and

(e) establishing the mechanical and corrosion properties of a 13% Cr martensitic SS and correlating the effects of various austenitizing and tempering heat treatments on its properties, including hydrogen embrittlement (HE).

*4.2.3.1. Grain boundary engineering*

Stainless steels, like 304L and 316L,though highly resistant to uniform corrosion, are prone to sensitization making them susceptible to IGC and IGSCC. Extensive research at Materials

Group, BARC has unequivocally shown that a very high concentration of random boundaries offers an effective means of improving resistance to both IGC and IGSCC in austenitic stainless steels [6].

With cold working, increase in the fraction of random boundary from about 30-40% in the AR condition to about 70-80% after 80% cold rolling(followed by controlled solutionizing) was observed. The degree of sensitization (DOS) increased with increasing random boundary concentration, but dropped significantly beyond a "critical" value irrespective of the type of rolling (e.g., unidirectional or cross rolling).These results show significant decrease in the DOS at high percentage of reduction and correspondingly high randomization of grain boundaries. Also, the IGC rates, were lower for the 80% cold rolled, annealed, and sensitized samples in comparison to samples cold worked for20-60% followed by annealing. These results have clearly shown that samples with a very high fraction of random boundaries have high resistance to IGSCC.

*4.2.3.2. Nitric acid grade of SS 304L*

The operating conditions in nuclear fuel reprocessing and nuclear waste management plants, which handle nitric acid, are highly oxidising in nature and at high operating potentials in the nitric acid streams, the corrosion rate of structural materials are high. Austenitic SS used for these applications exhibits several corrosion problems as these steels are prone to IGC also in nitric acid environments which is attributed to chromium depletion and segregation of elements like silicon and phosphorus at grain boundaries. Tubular products of stainless steels are also prone to *end grain corrosion* [7] which is observed in the exposed cross-sectional faces of materials that contained inclusions or have segregation of Si and P along their working directions.

The general corrosion rate in oxidising nitric acid environments is as important [8] as the IGC and end grain corrosion. The corrosion of SSs in strong oxidising nitric acid medium occurs due to the oxidation of the surface film, $Cr_2O_3$, to form chromic acid in the solution making environment more oxidising and aggressive. This phenomenonis observed in those components in which nitric acid fluids are recycled or not refreshed periodically, as the corrosion products would keep on accumulating increasing the oxidising power of the process fluid.

This understanding of corrosion in oxidising environments led to the development of a nitric acid grade (NAG) of stainless steel [8,9]. The type 304L NAG has been indigenously developed and now being used in the nuclear reprocessing plants and in applications handling radioactive waste dissolved in nitric acid. The key approaches used in the development of 304L (NAG) were [8]: (a) control of intergranular corrosion by controlling C, Ni, Si and P in the SS and resorting to lower grain size, (b) control of end grain corrosion by reducing inclusion content in SS, specifically by controlling Mn and S content, (c) reducing segregation of elements, specially P, at grain boundaries to avoid end grain corrosion in highly oxidizing nitric acid environment (in the transition to transpassive regime) and (d) control over uniform corrosion by minimizing the concentration of corrosion products that are in higher valence state. A small amount of cold work is also known to improve the corrosion resistance.

*4.2.3.3. Corrosion of non-sensitized stainless steels in high operating potential regimes in nitric acid service*

Stainless steels have inherent limitations in nitric acid environment. The limit of potentials upto which a given SS can be used without intergranular attack (even for a non-sensitized microstructure) can be varied either by chemical composition or by microstructural features like grain size and cold working effects.

A methodology was developed at BARC to study the corrosion of SS in boiling nitric acid environment and measuring/applying any given potential [10]. This novel methodology enabled the measurement of weight loss during the exposure test and in establishing if the corrosion attack was due to intergranular corrosion. This methodology helped in establishing the effects of variables, like chemical composition, grain size, microstructure (step/dual/ditch structure), inclusions etc., on the propensity of intergranular corrosion at any applied potential. In addition, the methodology allowed to simulated the role of fission products present in nuclear spent fuel reprocessing studies at an applied potential.

Establishment ofpotentio-dynamic polarization behaviour at various temperatures in different concentrations of nitric acid showed the existence of a threshold potential above which intergranular corrosion of a given SS takes place and below which only uniform corrosion occurs [11]. Higher threshold potential represents superior resistance to IGC. This fundamental work led to many profound observations for stainless steel in nitric acid service, including the effect of the effect of temperature, nitric acid concentration and presence of oxidizing ions on increasing the operating potential. At a given applied potential, intergranular corrosion rates are in the order of type310L < type 304L (NAG) < type 304L.The studies also showed that the grain boundary engineering is effective in transpassive regime of potentials.

*4.2.3.4. Improving resistance to IGSCC in simulated environment of NPP*

An extensive work to establish the basic mechanism of IGSCC and to improve the resistance to IGSCC in high temperature high pressure aqueous environment on type 304L SS with addition of nitrogen content [12] has shown that nitrogen addition of 0.12 wt% helped in improving the resistance to IGSCC in reactor operating environment [12]

*4.2.3.5. Martensitic stainless steels*

Martensitic stainless steels (MSSs), such as type 403, 410 and 420, are widely used in different industrial sectors including nuclear power industry. The mechanical and corrosion properties of these MSSscan be tailored by the heat treatments. Typical heat treatment cycle consists of annealing followed by austenitization (hardening) and finally tempering.

The effect of different tempering treatments on localized corrosion, mechanical properties and hydrogen embrittlement (HE) of 13wt.% Cr MSS (e.g. type 420 SS) which is used in Indian light water nuclear reactors was studied in-depth. Localized corrosion resistance (intergranular and pitting) in tempered MSSs was shown to be lower than that of austenitized condition with the least resistance shown by MSS tempered at 550 °C

Tempering affected the mechanical properties too. Drastic reduction in impact toughness with intergranular (IG) cracking at room temperature was observed after tempering in the temperature range of 500 to 600 °C and ascribed to temper embrittlement phenomenon. The results obtained in this study showed that the 13Cr MSS when tempered at 700 °C, provides optimum mechanical properties, moderate resistance to localized corrosion and HE.

*4.2.4. Reduced activation ferritic-martensitic steel*

Reduced activation ferritic-martensitic steels are the one of the proposed candidates for first wall structure in fusion reactors. Reduced activation is achieved by the selection of appropriate alloying elements and by controlling substitutional and interstitial impurities. Reduced activation ferritic-martensitic steel are the derivatives of the commercially available modified 9Cr-1Mo steel where constituents producing radioisotopes having long half-lives (e. g. Mo, Nb) have been replaced by relatively lesser active counterparts (like W, Ta). Several countries have developed their own reduced activation ferritic-martensitic (RAFM) steels. India has developed its own IN RAFM steel which has nominal composition as Fe-9.04 Cr-0.08 C-0.55 Mn-0.22-V 1.4-W 0.06-Ta. Detailed characterization of IN RAFM steel has been carried out and when this steel was compared with other RAFM steels showed its performance similar to other steels. Detailed studies on their interactions with Pb-Li, a proposed coolant for fusion reactors, has shown that IN RAFM perform slightly better than the other steels [13]. The Presence of W appears to provide stability to oxide layer which improves liquid metal corrosion of the steel. Detailed studies on liquid metal corrosion of the steel under various conditions have been carried out at BARC, leading to development of a detailed mechanism of corrosion and various methods of mitigation of the corrosion.

*4.2.5 Maraging steels*

Maraging steels have a mutually exclusive combination of high strength and high ductility, high concentration of alloying elements and good weld ability, multiple phases and high corrosive resistance. These properties in this steel are achieved by lowering the carbon concentration to 0.03%, which ensures bcc-martensite while the high strength in the steel is achieve by the precipitation of intermetallic phases like $Fe_2Mo$ and $Ni_3Ti$. Presence of several alloying elements in high concentration make the process of precipitation in these steels a very complex phenomenon and requires precious control over the aging treatment. Detailed studies on the precipitation process were carried out by Srikumar Banerjee and group [14] and not only many metastable phases were identified but their phase fields and crystallographic details were also determined. These details were used to generate crystallographic relations among them and sequences of phase transformations were established. Such studies have not only addressed several unresolved issues in the steel but also paved the way to design better maraging steels.

### ***4.3. Nickel Based Alloys as Structural Materials in NPPs***

*4.3.1. Alloys for Steam Generator tubing*

BARC has been working on all the three alloys (alloy 600, alloy 800 and alloy 690) to establish the sensitization behaviour, IGC susceptibility of the alloys after welding and to understand the mechanism of oxidation in SG, especially during hot conditioning of PHWRs (Fig.5).

In SG tubing materials, alloy 690 and alloy 800, heat affected zone (HAZ) formed due to autogenous welding is more susceptibleto IGC in comparison to any other part of the material, as these regions are exposed to the temperature regime of sensitization [15]. In the case of alloy 600,however, weld fusion zone (WFZ) was found to be more susceptible to IGC than HAZ. In laser welded condition, the DOS values for both WFZ and HAZ were comparatively lower than that in tungsten inert gas (TIG) weldments for all the alloys indicating that the higher heat input of TIG welding with slower cooling rates resulted in increased sensitization.

*4.3.2. Alloy 600: Improving the resistance to sensitization and IGC by grain boundary engineering*

Alloy 600 is known to be highly prone to sensitization and has high susceptibility to IGC; even in as-received annealed condition. Sensitization occurs when these alloys are exposed to a temperature range of 450 to 850 °C which led to the formation of Cr-rich carbides with concomitant Cr-depletion regions at the carbide-matrix interface regions. Alloy 600 is processed through suitable thermo-mechanical processing route to improve its resistance to sensitization/IGC resistance by increasing the percentage of low energy boundaries. The experimental results have shown that underas-received annealed condition the alloy is highly susceptible to IGC in boiling solution of ferric sulphate-sulphuric acid (G 28, ASTM test).

Various grain boundary engineering methods are used to improve the percentage of low energy boundaries to above 85%. This increase in fraction of low energy boundaries reduced the DOS values to 0.78% and 0.37%. Samples subjected to grain boundary engineering conditions showed no IGC attack in G 28, ASTM test, thus making the Alloy 600 resistant to IGC.

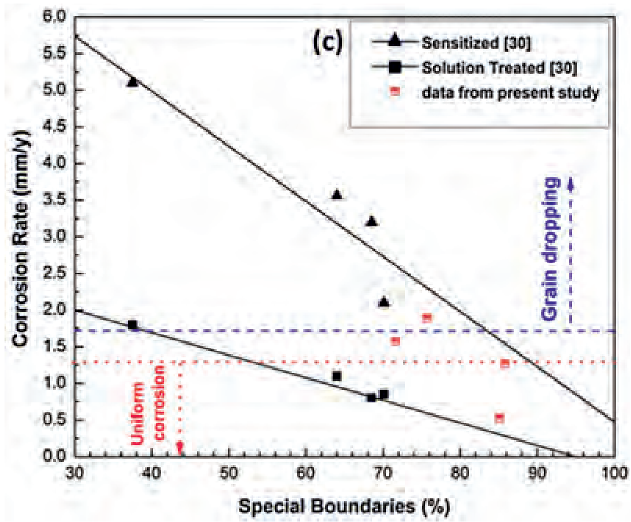



**Fig.5: Decreased corrosion rate as a function of increased fraction of special boundaries**

### *4.4. High Temperature Alloys*

There are classes of alloys which can be used at high temperatures. This broad category of alloys includes superalloys and alloys based on refractory metals. Superalloys are high temperature alloys which can be used at a high fraction of their melting points. These have several other important properties like very good mechanical properties particularly creep strength, and resistance to high temperature corrosion. The temperature range of application of the superalloys is limited to about 1300 C. However, these can withstand oxidising atmosphere very well and hence find application in different parts of gas turbine engines. These applications also require very high creep resistance which the superalloys are capable of showing. Most of the superalloys are based on Ni.

#### *4.4.1. Monel K 500*

Monel family of alloys are Ni-Cu based alloys where their ratio is kept close to 70:30.Alloys of this family are known for their corrosion resistance in a variety of environments and hence find application in marine fittings, oil well drilling collars, pump shafts, impellers, condenser tubing etc. Monel K 500 is a precipitation hardenable alloy The alloy has small amounts of Al, Fe, Mn, S, Si and C which provide this alloy a good combination of strength and excellent corrosion resistance even in very aggressive environments like hydrogen embrittling condition or sulphide stress corrosion environment. Dey *et al*. showed that in this alloy the precipitation occurs by the classical homogeneous nucleation process with the precipitates maintaining their coherency and spherical morphology even after prolonged ageing. Dey *et al.* [16] have also examined the structure property correlation in this alloy at different temperatures and have shown that the alloys shows all test book features a typical precipitation hardenable alloys.

*4.4.2. Alloy 718 and 625*

Alloy 718 and alloy 625 are superalloys which have excellent combination of high temperature mechanical properties including very good creep resistance and corrosion resistance in hostile environment. these alloys derive their strength from metastable, ordered g" phase (tetragonal $DO_{22}$ structure) [17]. This structure is based on the composition $Ni_3Nb$. Since this phase contains substantial amount of Nb, these superalloys contain a good amount of Nb. Due to the fact that" phase is a meta-stable phase, there is tendency for the stable $Ni_3Nb$ phase to form which is the delta phase. The formation of this phase in a controlled manner leads to an improvement in the stress rupture ductility. On the other hand, formation of this phase in the coarse form in large amount leads to degradation of strength of the superalloys. In India, these alloys are produced by MIDHANI. Alloy 625 is used very extensively in Heavy Water plants.

***4.5. Refractory-Metal Based Alloys***

Niobium (Nb), tantalum (Ta), molybdenum (Mo), tungsten (W) and rhenium (Re) are mainly designated as refractory metals, based on their high melting points (>1925C). Except Re, their common areas of application are in steel industry and production of sintered carbide tools in the form of respective ferroalloys and carbides, respectively. Specific application such as that of niobium in the field of metallic superconductor and nuclear reactor, tantalum as miniature capacitor and tungsten as incandescent filament, molybdenum as heating element and cathode support and rhenium as alloy softener bestowed them prominent recognition. Refractory metals and their alloys are capable of meeting an environment aggressive with respect to radiation, temperature, corrosion (gaseous and liquid metal) and stress for prolonged period. These materials are therefore, being considered as high temperature structural materials, for new generation reactors like accelerator driven system (ADS), high temperature reactor (HTR), fusion reactors and reusable launch vehicles. Conventional superalloys containing nickel, cobalt or iron–nickel as the major constituents, meet restricted high temperature applications and fail to qualify the benchmark of aerospace and nuclear industries. Beyond 1200K, the refractory metal-basedalloys are the only candidate materials for structural purposes.

The technology for aluminothermic reduction of the respective oxides ($Nb_2O_5$, $Ta_2O_5$) to produce massive forms of niobium and tantalum metals was developed at BARC. The thermit metal is further refined and consolidated using electron beam melting in which purification is done by vacuum degassing, carbon deoxidation and sacrificial deoxidation mechanisms. Technology for the production of capacitor grade Aluminothermic reduction reactor was specially designed for making thermit vanadium with low amount of nitrogen, and subsequent electron beam melt refining. These metals were also produced by molten salt electroextraction using metal carbide as anode feed. The process flowsheet has also been established on laboratory scale at BARC to recover several refractory metals from low grade indigenous sources and various secondary sources. The flow sheet for low grade wolframite concentrate was developed with the objective of recovery of tungsten and other valuable associates. Process knowhow was established for producing tungsten metal powder by hydrogen reduction of $WO_3$.

*4.5.1. Niobium based alloys*

Niobium based alloys exhibit good combination of high temperature strength, chemical compatibility with most liquid metals, relatively easy fabricability, and stability under nuclear environments. Due to these unique properties, Nb alloys have found many applications ranging from structural components in space nuclear reactors, high temperature reactors, aero-space engine and several biological applications. An alternate process consisting of aluminothermic co-reduction of mixed oxides followed by arc and electron beam melt refining was developed for preparation of Nb-1Zr-0.1C alloy at Materials Group, BARC. The ingots of the homogenized alloy were produced after electron beam melt consolidation The lower deformation temperature (800°C) also provides an opportunity to jacket the material with Cu (Fig. 6). A high temperature liquid Lead-Bismuth Eutectic (LBE) loop named as kilo temperature loop (KTL) made of Nb-1Zr-0.1C alloy was set up in BARC for thermal hydraulics, instrument development and material related studies relevant to compact high temperature reactor(CHTR) [18]. The loop was operated up to 1100ºC using natural circulation of molten LBE, and the potential use of the Nb-1Zr-0.1C alloy for high temperature reactor was demonstrated.

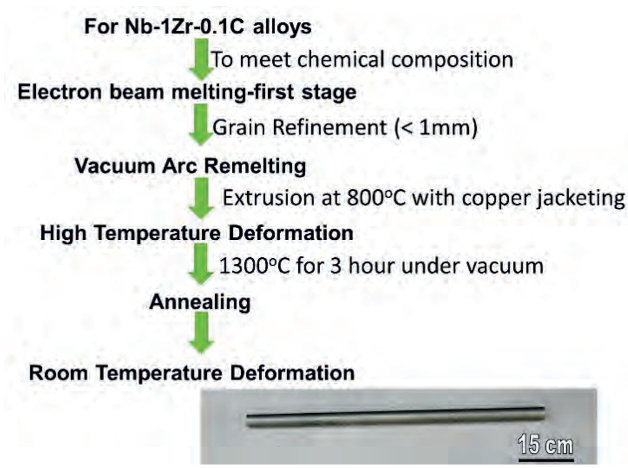



**Fig. 6: Flow sheet showing processing of Nb. In the inset fabricated tube is shown.**

*4.5.2. Vanadium based alloys*

Attractive properties of vanadium alloys, such as low neutron activation, superior resistance to irradiation swelling, low helium generation, superior liquid metal corrosion resistance, moderate thermal conductivity, and adequate mechanical strength make them potential candidates for structural applications in nuclear fusion and fast fission reactors. V-4Cr-4Ti alloywas identified as the structural material for fusion reactors operated in the temperature regime of 400-700°C. The temperature limit of the operational window of V-4Cr-4Ti alloy is majorly limited by the reduction in the strength and the issues related with helium embrittlement at elevated temperatures (exceeding 700°C). Addition of Ta as an alloying element in V-Ti system could improve the capability of the alloy for higher temperatures.

*4.5.3. Tungsten based alloys*

Tungsten has high melting point (3410°C), high density (19.26 g/cm$^3$) and superior mechanical strength at high temperatures. Tungsten metal is being considered to be used as plasma facing components of fusion reactors (ITER). Tungsten based heavy alloys (WHA) such as W-Ni-Fe and W-Ni-Cu possess distinguished properties with respect to absorbing radiation, mechanical strength and machinability. These are the ideal materials for a wide range of applications, such as in aerospace, the automotive industry, medical engineering and the construction industry. Different shapes of WHAs are used as gamma radiation shielding in the cancer therapy machines such as Bhabhatron. WHAs are used in the kinetic energy penetrators for military application.Technologies were demonstrated for preparation of pure tungsten metal powder and its subsequent consolidation by vacuum hot pressing. The components of WHA (W-2Ni-1Fe) were fabricated using liquid phase sintering approach and the product showed the desired mechanical properties and targeted density [19].

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