11. ENGINEERING - MATERIAL RESEARCH

INTRODUCTION

This chapter covers the research and development activities on the materials of importance for the development of nuclear reactor technology. These activities cover various aspects of materials research ranging from the development of processes for extraction, fabrication routes for optimisation of material properties, characterisation of materials for newer alloys by micro-structural studies etc.. Along with this, various studies related to degradations and failure mechanisms under the application environment are also being carried out to characterise as well as optimise the performance of these materials.

This chapter gives a brief description of all such activities mentioned above and provides the readers with an option to probe further into the topic of their interest by contacting respective author(s).
11.1 CHARACTERISATION AND DEVELOPMENT OF NEW CLADDING ALLOYS

The future PHWR reactors with higher coolant temperatures, higher burn ups and partial boiling condition operations will require development of newer cladding alloys.

- **Study of the influence of controlled additions of interstitial and substitutional alloying elements for optimum microstructure and properties of the alloy**

Several studies on the binary Zr-1Nb and the quaternary Zr-1Nb-1Sn-0.1Fe alloys have shown superior corrosion resistance and irradiation creep for the cladding applications in comparison to existing alloys. Based on these observations a series of Zr-Nb (Nb varying from 0.5 to 1.5) alloys with systematic addition of Sn and Fe have been prepared with varying oxygen content. Microstructural characterization of these alloys has been accomplished using optical, scanning and transmission electron microscopy.

- **Study of the range of possible metallurgical treatments for chosen alloy systems**

The microstructures of Zr-based alloys are generally very sensitive to thermo-mechanical treatments. The quenched and tempered microstructures of these alloys have been studied. The annealing study of a binary and quaternary alloy has been completed. The microstructures of cast specimens of the two new alloys, Zr-1Nb-0.8Sn and Zr-1Nb-1Sn, showed a needle-like Widmanstatten structure. The needles of the α-phase were found randomly oriented within the grains and a second phase was seen segregated at the plate boundaries. The hot rolled microstructure showed evidences of dynamic recovery occurred during the process of deformation at a temperature above the recrystallization temperature. Presence of smaller, defect-free and equiaxed grains formed during recrystallization process were observed in TEM micrographs. However, evidences of partial recrystallization were noticed as the needle like Widmanstatten structure was retained in various parts of the samples used for metallographic examination. The process of β quenching resulted in the martensitic transformation and as a result of this the β phase present in the specimen was transformed to martensite. The microstructure showed sharper and longer laths. Also, the stress associated with the martensitic transformation resulted in the formation of twin related laths.

- **The performance of these optimized alloys in terms of corrosion resistance, hydriding, mechanical properties and irradiation creep is planned to be studied.**

Hydriding studies of binary Zr-Nb alloys have been completed. Hydriding studies were carried out on Zr-2.5Nb and Zr-1Nb alloys to understand the mechanism of hydride formation in dilute Zr-Nb alloys. TEM studies have shown that in both the alloys δ-hydride is formed in the slowly cooled samples and γ-hydride is formed in the rapidly cooled samples. In both the alloys acicular morphology of hydride plates was predominantly observed. In case of the Zr-1Nb alloy a zigzag morphology of the δ hydride was seen in samples containing higher concentration of hydrogen. Occasionally internally twinned hydride plates were observed only in the case of Zr-2.5 Nb. In this study it has been seen that the hydride plates disregard the α/α as well as α/β interfaces. The orientation relationships between the α and the δ hydride phases is (0001)α//(111)δ and [1120]α//[(110)δ] and between the α and the γ hydride phases is (0001)α//(111)γ and [1120]α//[110]γ. These orientation relationships were found to be identical in both alloys. In the case of α to γ hydride formation, it was seen that the habit plane predicted by the phenomenological theory of martensitic transformation matches exactly with the experimentally determined value.

- **Development of fabrication flow sheet**

A collaborative work with NFC is being pursued where evolution of microstructure during different stages of fabrication of cladding tubes will be assessed and correlated with the properties. Based on these studies an optimized fabrication flow sheet will be developed for cladding tubes with reproducible microstructure and properties.
Texture and Microtextural study in Zr-base alloys:

Texture development in two phase Zr-2.5Nb alloy

Development of the deformation texture was noticeable in single-phase (hcp $\alpha'$) regions, but insignificant in two-phase (hcp $\alpha$ and bcc $\beta$) regions. Taylor type deformation texture models could predict the texture changes in single-phase microstructure, but cannot explain lack of change in two-phase Zr-2.5Nb alloy.

The majority of the two-phase structure consists of Widmanstätten $\alpha$ in a $\beta$ matrix. Deformation in such regions was restricted to softer $\beta$. Uni-directional rolling aligned the $\alpha$ plates along rolling direction and only on rolling plane, but individual $\alpha$ plates remained nearly single crystalline. No macroscopic strain was present in $\alpha$ plates and significant hardening of $\beta$ was observed. In-Plane Rigid Body Rotation of $\alpha$ plates in an apparently continuous $\beta$ matrix possibly explains absence of quantitative texture development in rolled two-phase alloy.

Effect of Texture on Hydriding

Precipitation of Hydrides may lead to reduced ductility, transition from ductile to brittle fracture and premature failure due to Hydrogen Induced Delayed Cracking (HIDC). The harmful effects of these hydride precipitates depend on many factors - such as relative amount, distribution and morphology of the hydride phase. The presence or relative formation of hydrides is expected to depend strongly on the structural parameters – crystallographic texture, microstructure/microtexture and residual stress anisotropy. The relative role of such structural parameters on the formation of hydrides is being studied. Different Zircaloy-2 samples (obtained from different stages of Zry-2 tube fabrication) with different bulk crystallographic textures and anisotropy in residual stresses were hydrided to 200 ppm of hydrogen. These formulated the materials for detailed structural characterization. The hydrides as observed in OIM (Orientation Imaging Microscopy) scans, in general, were along the grain boundaries – possibly ruling out a ‘direct’ role for bulk crystallographic texture. Identification of hydride forming boundaries was attempted to determine the possible role of grain boundary nature on the hydride formation. The study of the elastic stiffness from the orientation data, on the other hand, was aimed at bringing out
the role of elastic deformation and to link the hydride formation with macroscopic values of anisotropic distribution in residual stresses.

Microstructural studies of Irradiated RAPS Pressure Tube Material

It is known that microstructure controls the material properties, thus, it is important to understand the structure-property relationship during irradiation of the material. Unlike cubic material, there are not many investigations available for hcp metal and alloys like zircalloys. In this study, samples from the pressure tube exposed for 6.7 effective full year from the high flux region of the RAPP-I reactor were obtained. These tubes were exposed to the total cumulative damage in the range of 2.5-3 dpa.

The microstructure of the irradiated samples was different in many respects in comparison to the microstructure of the unirradiated samples. The presence of defect structures in the form of dislocations-loops, dislocations array etc. could be seen in the irradiated sample. These loops were mostly c type loops lying in the basal plane. The refinement and alignment of the precipitates in a particular crystallographic direction were indicative of this fact that the dissolution and redistribution of the precipitates had occurred in the irradiated samples. In the present case amorphisation of any precipitate could not be confirmed. The irradiated structure did not suggest extensive recovery of the structure as reported in other investigations. The hydride needles were also observed in the irradiated samples, however, in this case the morphology of the ‘a` matrix had changed. They did not show any sharp interface as normally seen in the unirradiated samples.

11.2 STUDIES ON PH 13-8 Mo STEEL

Alloy PH13-8Mo is a precipitation hardenable martensitic stainless steel, which has strength and toughness superior to 17-4PH steel and is used in various components such as ‘ball-screw’ and ‘seal disc’ of 500 MWe PHWR. The mechanical properties, e.g. strength and toughness of this alloy are derived, to a great extent, through the development of microstructure and specifically through the precipitation of fine, coherent β-NiAl ordered phase on aging of solution-quenched structure at temperatures ranging from 783 K to 893 K. Studies on the microstructure of solution-quenched PH13-8Mo steel, aging kinetics of β-NiAl formation and the effect of grain size on the mechanical properties are conducted to find out the structure-property correlation in this steel.

The solution-quenched structure of PH13-8Mo is important, since, this structure is further aged to obtain various combinations of strength and toughness in the material. In this study solution-quenched microstructure of wrought PH13-8Mo steel was investigated by Transmission Electron Microscope (TEM) and Small-Angle Neutron Scattering (SANS). It was found that the needle shaped austenite (γ), as shown in figure was retained in the quenched structure when the alloy was subjected to fast quenching after austenitizing at high temperature. The retained austenite was seen to maintain Kurdjumov-Sachs type relationship with the martensite (α’). The blocky primary carbides, as shown in figure was confirmed, with the help of Energy Dispersive Spectroscopy (EDS), to be rich in Mo and Cr. These carbides were found to contribute strongly to the SANS signal and their shape and size were modeled with the help of software figure. While presence of retained austenite softens the solution-quenched stainless steel, the primary carbide may affect the precipitation of NiAl ordered phase and hence the property of the alloy.

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Nucleation and growth kinetics of $\beta$-NiAl precipitation in wrought PH13-8Mo stainless steel was evaluated using Avrami formalism. For this, different solution quenched samples were aged at 783 K, 808 K, 840 K and 868 K, respectively, for durations ranging from 180 s to 86400 (24 h). Activation energies of $\beta$-NiAl precipitation at 75 % and at 90 % transformation in wrought PH13-8Mo, respectively, was calculated to be 126.7 kJ/mol and 188.17 kJ/mol. This indicates that the nucleation is faster than the growth and helps to explain the highly-resistant-to-coarsening nature of $\beta$-NiAl precipitates. The analysis further indicates nucleation of $\beta$-NiAl precipitates along or near dislocations, followed by needle or plate like growth helped by dislocation-aided diffusion.

Correlation between toughness and grain size in PH13-8Mo Steel.

To study the effect of grain size, PH 13-8 Mo stainless steel samples from three different batches of melt were subjected to solutionizing at 1223 K for 30 minutes followed by quenching. The quenched samples were aged at 783 K (950 °F). While all samples achieved specified strength, % elongation and hardness, only one sample that had smallest and uniform grain size in the longitudinal and transverse direction could achieve the specified toughness value. Composition analysis indicated that all samples conformed to that of PH 13-8 Mo stainless steel. The correlation of toughness with the grain size is shown in figure. Hence, small and uniform grain size appears to be an important factor to achieve the right combination of strength and toughness in this steel.

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11.3 REFRACTORY METALS AND ALLOYS FOR ADSS, AHWR AND CHTR

Refractory metals and alloys such as Nb-1Zr, Nb-1Zr-0.1C, TZM, Mo-30W, Ta-10W, etc. are capable of withstanding an aggressive environment with respect to radiation, temperature, corrosion (gaseous and liquid metal) and stress for prolonged period. These alloys are potential candidate materials for new generation reactors, viz. ADSS, CHTR and AHWR. The process adopted for preparation of these alloys consists of aluminothermic co-reduction of the mixed oxides in the presence of judicial proportion of additives to result in a consolidated alloy product well separated from the slag. As prepared alloy is further subjected to homogenization in an arc melting furnace and finally refined by electron beam melting. Charge composition (0.1kg scale) used for the preparation of a
selected few refractory metal-based alloys and the results are summarised in table. An optical microstructure of Mo-30W alloy revealing large grains of about 200-300 μm is presented in Figure.

Refractory metals and alloys have low oxidation resistance which restricts their application at elevated temperatures. Proper oxidation resistant coatings need to be developed to circumvent this limitation. Silicide, aluminate and or alumino-silicide type of coating are reported to be well suited for high temperature applications.

Amongst a large number of coating techniques, Halide Activated Pack Cementation (HAPC) process has been taken up to form single and multilayer coatings. The HAPC method is a diffusion coating process that involves embedding the substrate into a sealed or vented refractory container with a powder mixture called the pack (Al or Si + NH₄F or NH₄Cl + Al₂O₃), which is then heated at 1173-1473K in an inert surrounding atmosphere for 8-24 hours. In the process halide activator (NH₄F/NH₄Cl) decomposes at high temperature to produce volatile halide vapours of the master alloy (Al/Si) elements. The chemical potential gradient between the master alloy and the substrate drives gas phase diffusion of the metallic halides to result in surface deposition.

50 to 60 μm thick coating could be obtained on different refractory metal-based alloys. The SEM image of coated surface of TZM alloy reveals that the coating is smooth and granular. In the microstructure of coating cross section on TZM, no cracks were observed in the coating layer. The two types of layers, present in the coating, the outer layer consists of the ternary intermetallic phase of Mo(Si, Al)₂ and the inner layer of MoSi₂ phase.

X-ray line scans showing distribution of Mo, W, Si, Al across the interface.
11.4 DEVELOPMENT AND MICROSTRUCTURAL STUDIES OF Cu-1Wt%Cr-0.1Wt Zr ALLOY FOR THE FIRST WALL OF TOKAMAK

Dilute Cu-Cr-Zr alloys and their minor modifications, because of their high thermal conductivity, high strength and high resistance to fatigue at 723 K, find applications in high technology areas like yet-to-be-commercialised tokamak. Cu-1 wt % Cr-0.1 wt%Zr is used to fabricate diverter plates and heat transfer elements and is also likely to be employed as a heat sink in the first wall of future torroids. Elsewhere in the world, this alloy has been developed and studied quite exhaustively but some aspects like orientation relationship of the nucleating precipitates with the matrix and role of zirconium in imparting fatigue resistance have remained controversial. At BARC, an attempt was made to develop and study this alloy and carry out its electron beam welding to stainless steel and its diffusion bonding to tungsten as well as stainless steel— all this with new interesting results that are described below.

The distribution profiles of Al, Si, Mo and W at the interface between the coating and the matrix of Mo-30W alloy, indicate that the outer layer contains very high amount of aluminium with slight variation in percentage and the inner layer consists of (Mo, W)Si₂ type of intermetallic phase.

Coated samples were tested for their oxidation resistance by heating initially to a temperature of around 1000 K and finally to 1300 K for 24 hrs. in dry air. The samples were found to withstand tested temperature without suffering from oxidation.

Preparation of refractory lining, its regular maintenance and likely contamination of the product from the refractory lining are the limitations of refractory lined reactor used in the reduction campaign. It has been planned to replace refractory lined reactor with a refractory less reactor having provision to operate under an inert atmosphere to overcome the above cited limitations as well as to prevent pick-up of the impurities from the open atmosphere. Mixed oxide reduction campaign on kilogram scale would be initiated using open top refractory lined reactor by the beginning of 2007.

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11.5 ZIRCONIUM ALLOYS AND MODIFIED 9Cr-1Mo FERRITIC STEEL

Fabricability of a Modified 9Cr-1Mo Ferritic Steel

The modified 9Cr - 1Mo (T 91 grade) steel was developed over the years by steel makers with an aim to meet requirements of SG pipes and headers in boilers as a substitute to austenitic stainless steels and was found to have good void swelling resistance under fast neutron environment. Though, the available data suggests that the modified 9Cr-1Mo steel has excellent fabrication properties and adequate long term strength, it is still necessary to get a few field trials before it can be accepted as the substitute material for high temperature use. The aim of the present investigation will be to evaluate the fabricability aspects of this steel at room and elevated temperatures. This evaluation is done by estimating the mechanical properties under different microstructural conditions. Deformation behavior was studied from 77 to 1273 K under these microstructural conditions. The results were analyzed using existing deformation models and the deformation mechanism is classified in strain-rate, strain and temperature space.

Studies on Zirconium alloys

Two series of alloys, which have found extensive applications as in-core structural materials of nuclear reactors, are zircaloy and Zr-Nb alloys. Though both the alloys have given reasonably good performance, efforts are being made to modify composition and microstructure and to understand in-service degradation mechanisms so as to obtain enhanced performance. Studies related to safety issues of concern viz., creep deformation, deformation behavior under accidental conditions and hydrogen/hydride induced degradation of mechanical properties are being presently pursued at the Materials Science Division.

Deformation behavior of Zr-alloys

In Pressurized Heavy Water Reactor, Zr-2.5Nb tubes serve as miniature pressure vessels operating at about 573 K, with a coolant pressure of ~ 10 MPa. In order to understand and predict the deformation behavior of this alloy under accidental conditions.
conditions, deformation behavior was characterized by uni-axial tension tests at temperatures between room temperature and 1073 K as a function of specimen orientation, test temperature and strain-rate. Results showed that both yield and ultimate tensile strengths of this alloy decreased with increasing test temperatures, with a rapid fall in strengths above a temperature of 623 K. The alloy exhibited extensive superplasticity (ductility exceeding 100 %) in the temperature range of 923 – 1073 K and under optimum conditions it exhibited a ductility value of approximately 950 %.

Hydride embrittlement of Zr-alloys:

The hydrogen absorbed by Zr-alloy tubes during their service precipitates as brittle hydrides once their Terminal Solid Solubility (TSS) is exceeded and results in deterioration in their mechanical properties. TSS of hydrogen in both zircaloy-2 and Zr-2.5Nb alloy was determined using dilatometry technique as a function of temperature, direction of approach of temperature and microstructural condition. Further, it was demonstrated that the tensile and fracture toughness properties of Zr-alloys, studied in the temperature range of 300 to 573 K using a direct current potential drop technique are a strong function of the orientation of the hydrides. A benignly oriented hydride precipitate, under the influence of external stress, can undergo a change to a less favorable orientation at stress levels beyond a threshold value under suitable conditions. Threshold stress for reorientation of hydrides was determined for Zr-2.5 wt. % Nb pressure tube material in the temperature of 423 – 723 K and the effect of the reoriented hydrides on the tensile properties was determined in the temperature range of 298-573 K. A theoretical model of reorientation, based on the packing density difference between the grain-boundary and the grain, was proposed to explain the basis of reorientation of hydrides in this alloy.

The dissolved hydrogen migrates up the hydrostatic stress gradient and can accelerate the fracture process (Delayed Hydride Cracking, DHC). Based on a comparative study on the DHC velocity in CWSR (Indian, Canadian) and quenched and aged (RBMK) Zr-2.5Nb pressure tube alloy, the concept of threshold hydrogen concentration for DHC initiation and propagation was proposed. The variation in the DHC velocity for initiation and propagation with temperature was computed and it was suggested that DHC couldn’t take place below a certain limiting hydrogen concentration.

Another manifestation of localized embrittlement, caused by hydrogen migration down the temperature gradient, is the formation of hydride blisters at cold spots. The morphology of blisters and their microstructural details were systematically studied in a Zr-2.5Nb pressure tube material. The computed stress field around a hydride blister, grown under controlled thermal boundary conditions could explain the hydride platelet orientation in the matrix surrounding the blister. Experiments are under way to determine the cracking strength of blisters and influence of presence of blisters on mechanical properties.

Influence of hydrogen on creep deformation in Zr-alloys

The creep rate and the applied stress can be related through empirical relations involving many microstructural parameters. The objective of this work was to bring out the importance of empirical relations in distinct stress ranges and to show the failure of simple linear extrapolation of the creep rate from one stress range to another while predicting creep rate. The creep data of Zr-2.5Nb and modified 9Cr-1Mo steel were used as illustrative examples to demonstrate the use of single specimen short term tests (at a fixed temperature) as supplementary to conventional creep tests using multi specimen long term tests. The limitations of extrapolation of creep data from one stress range or metallurgical condition to another were also demonstrated. Based on these results it was further possible to demonstrate that the creep rate increased with hydrogen addition while the stress exponent and mechanism of creep deformation remained unaffected.

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water chemistry similar to BWRs, the issue of Stress Corrosion Cracking (SCC) of these components has to be addressed. Ensuring absence of sensitisation and Low Temperature Sensitisation (LTS) over the complete design life of the components will ensure freedom from early onset of IGSCC. However, there is no data to assure that LTS will not take place in 100 years of operation at around 300°C.

All the IGSCC failures in recirculation pipelines of BWRs have occurred at the heat affected regions of weldment and not elsewhere in the base material. It has been shown that there is a residual strain of 15-20% in the region between the weld fusion line and the heat-affected zone (HAZ). Since all the LTS related cracking have been in this region, it is pertinent to study the LTS behaviour of stainless steels which are in cold-worked condition. In a recent work completed last year, it has been shown that cold work has an important influence on LTS behaviour of stainless steels. Types 304/304L/304LN/316L/316LN were used for LTS studies in solution annealed/fabricated conditions with or without different degrees of cold rolling. Modes of deformation/working encountered during fabrication of stainless steel components were also investigated viz. cold rolling, bending, machining/grinding, warm working. The Degree Of Sensitization (DOS) was measured using electrochemical potentiodynamic reactivation (EPR) technique. It was shown that cold worked materials heat-treated at 500°C for 11 days do not always result in LTS but the mechanism changes to sensitisation with newer chromium rich carbides precipitating at grain boundaries. Therefore, extrapolation of the results obtained at 500°C to the behaviour at 300°C (500°C for 11 days as equivalent to 300°C for 100 years) is not valid. It was also shown that type 304 L and 304 stainless steels have a tendency to transform into martensite upon cold rolling. The martensite phase sensitised very fast (in a few minutes) between 300 to 500°C. This changed the LTS behaviour completely from that of an all-austenitic stainless steel and is shown in Figure. Similarly, on samples of type 304 that were bent by 90° showed accelerated LTS kinetics due to retained strain in the material.

The influence of Low Temperature Sensitisation (LTS) on the Degree Of Sensitisation (DOS) in two grades of 304LN stainless steels with 0.12 and 0.15 wt.% nitrogen were evaluated. A heat treatment at 500°C for 11 days was used to simulate LTS for 100 years at 300°C. The constant strain samples in annealed, sensitised water chemistry similar to BWRs, the issue of Stress Corrosion Cracking (SCC) of these components has to be addressed. Ensuring absence of sensitisation and Low Temperature Sensitisation (LTS) over the complete design life of the components will ensure freedom from early onset of IGSCC. However, there is no data to assure that LTS will not take place in 100 years of operation at around 300°C.

The effect of prior cold working (15% reduction in thickness) on the extent of low temperature sensitization (after 500°C heat treatment for 11 days) for various austenitic stainless steels. SS 304LN1 has 0.12% nitrogen and SS 304LN2 has 0.15% nitrogen.
and LTS treated conditions were used in the SCC tests. In the first SCC test the specimens were exposed in a boiling solution of acidified NaCl as per G 123, ASTM. In the second test, the specimens were exposed in a recirculating loop in oxygenated water at 280°C and 8 MPa for 1000 hours. A similar test was done with high purity water (specific conductivity 0.055 μS/cm). It was shown that 304LN with 0.15 wt.% nitrogen is more susceptible to sensitisation and LTS. For comparison, sensitised 304 samples were also exposed in the test using high purity water. While the sensitised 304 showed intergranular cracking (shown in the figure), the DOS developed in the annealed materials after the LTS treatment was not sufficient to make it susceptible to intergranular stress corrosion cracking. However, type 316LN stainless steel was found to be the most resistant grade of stainless steel to LTS. Even after 20% cold rolling, the 500°C heating for 11 days could not increase its DOS.

Complete intergranular cracking of the sensitised type 304 stainless steel in 400 hours of exposure to high purity water at 280°C. The figure shows (a) intergranular facets of the fracture surface and (b) secondary intergranular branches emanating from the main intergranular crack.

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11.7 STUDIES ON STRESS CORROSION CRACKING AND CORROSION FATIGUE BEHAVIOUR OF STAINLESS STEEL

Duplex Stainless Steels (DSS) exhibit higher resistance to localised corrosion as compared to the single phase austenitic stainless steel but under certain conditions it may become susceptible to hydrogen embrittlement. Susceptibility of DSS to hydrogen embrittlement was studied using the Slow Strain Rate Test...
At high applied $\Delta K$ regimes, the FCGR values didn’t have any appreciable difference indicating mechanical failure to be dominant with very little influence of the environment. Electrochemical tests on solution annealed DSS indicated that no pitting occurred even at very high applied potentials. Hence pitting was ruled out as a precursor to fatigue crack growth.

Though SS 304 is a workhorse in the stainless steel family, its application in sea water is limited to a great extent due to its proneness to localized corrosion. In the sensitized condition very dilute quantities of thiosulphate are sufficient to cause SCC in presence of residual/applied strain. It is prone to SCC in the presence of very small quantities of thiosulphate which may be formed due to the presence of sulphate reducing bacteria. Tests were carried using the Slow Strain Rate Test (SSRT) technique. Results of SSRT tests at room temperature indicated that sensitization and thiosulphate concentration greatly increased the susceptibility to SCC. Intergranular SCC was observed in solutions containing as low as 5 ppm thiosulphate. Experiments were also carried out at various applied potentials and current transients were observed to occur which corresponded to crack nucleation. Results indicated that film rupture and dissolution was the most likely mechanism of SCC.

Initial studies on FCGR/SCC have been carried out at room temperature. However, most of the engineering materials used in plants experience high temperatures and pressures in various aqueous environments. FCGR data available under such conditions will be of great significance. An experimental facility to carry out fatigue/SCC studies in environments at elevated temperature and pressure is planned to be set up. Such fatigue/SCC studies can be carried out in various conditions of applied potentials and water chemistry. Various reactor components operating under such conditions will be studied in such a setup. Crack growth will be monitored using the reversible DCPD technique. Testing facility for carrying out the tests under flowing conditions is also planned to be setup to simulate the conditions experienced by the materials in actual service.

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### 11.8 Fracture Behaviour of Zirconium Pressure Tube Alloys: Effect of Hydrogen and Impurities

The fracture toughness of the fabricated cold worked or annealed pressure tube materials is influenced primarily by the microstructure, texture and flow strength, as fabricated alloys show typical ductile fracture over temperature range of interest. However, severe degradation in the fracture toughness is observed due to irradiation hardening and hydrogen/deuterium absorption during service mainly from the corrosion processes. The effect of hydrogen on the performance of the component is reflected in the change in fracture behaviour and/or by its role in the delayed hydride cracking behaviour. Hydrogen embrittlement in zirconium alloys depends primarily upon the amount of hydrogen present in the matrix, morphology, orientation and distribution of hydrides and the texture, strength and fracture toughness of the zirconium matrix itself.

This work, using unirradiated samples, has generated a database, which can be referred for assessing the toughness level of the pressure tube materials (Zircaloy-2 and Zr-2.5Nb) as a function of the hydrogen content. Through a systematic study, it was also possible to suggest a test procedure for generating the entire J-resistance curve from a single sample at temperatures greater than transition temperature. This minimizes the number of tests required for fracture toughness measurement on samples of irradiated pressure tubes at elevated temperatures. In the sections to follow the salient features of the new test method adopted for this data generation and some important experimental observations on the effect of hydrogen and impurity segregation are given.

A new methodology for characterizing fracture behaviour by load normalization method, which is based on the Key Curve approach, has been established. This method does not need any on-line crack-monitoring unit. It uses single specimen load – Load Line Displacement (LLD) record for the evaluation of J-R curves for Zircaloy-2 pressure tube material with different hydrogen content (10, 60, 110 ppm) at different test temperatures.

J-R curves for Zr-2.5Nb Alloy charged with 50 ppm of hydrogen at different test temperatures.

J-R curve. This new technique has been used to characterize fracture behaviour of both Zircaloy-2 and Zr-2.5Nb pressure tube materials over a range of temperature and hydrogen content. This method compares well with the conventional ASTM test methods. Figure compares J-R curves obtained by this method.
toughness of hydrided material slowly increases with increase in the test temperature up to 150°C and above 150 to 170°C a sharp increase in the toughness value is observed. The Quadruple Melted (QM) material containing lower amount of chlorine showed better fracture properties than DM material.

It is seen that the fracture toughness of Zr-2.5Nb pressure tube material can be improved substantially by reducing the level of trace element impurities like carbon, phosphorus and chlorine. Chlorine content reduces from 2.5-5 ppm in DM condition to around 0.5 ppm in QM condition. It has been demonstrated at Nuclear Fuel Complex, Hyderabad that such a purity can be routinely achieved by quadruple vacuum arc remelting practice. Fractographic investigation revealed the presence of linear low energy fracture channels and aligned second phase precipitates in double melted alloys (Cl ≈ 2.5 ppm), which were absent in quadruple melted alloys (Cl ≈ 0.5 ppm). These results show that control of trace impurities is essential as it results in substantial increase in the crack growth toughness (dJ/da values) coupled with improved initiation toughness and reduced scatter in toughness levels. An additional benefit from quadruple melting is reduced hydrogen level as in fabricated tubes, which come down to 4 to 5 ppm in quadruple melted tubes from the 10 to 15 ppm level in the double melted alloy. Considering the critical role of hydrogen in pressure tube material, this may give a substantial increase in the pressure tube service life.

Hydride embrittlement studies in the Zr-2.5Nb pressure tube have been carried out over a range of temperature and hydrogen content ranging from 25 ppm to 60 ppm, as fabricated pressure tubes obtained from double melted (DM) ingot, when charged with different levels of hydrogen show sharp reduction in fracture toughness values at ambient temperature. It is seen that the fracture toughness of hydrided material slowly increases with increase in the test temperature up to 150°C and above 150 to 170°C a sharp increase in the toughness value is observed. The Quadruple Melted (QM) material containing lower amount of chlorine showed better fracture properties than DM material.

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11.9 RATCHETING BEHAVIOUR OF PRIMARY HEAT TRANSPORT PIPING STEELS

Ratcheting has been defined as accumulation of strain due to asymmetrical stress cycling in materials. The phenomenon is potentially dangerous, because for a suitable combination of mean and cyclic loads, there can be continuous cycle-by-cycle plastic deformation. This contributes to the development of unacceptably large strains in the component. PHWR and AHWR have extensive piping layout to provide for heat transport. Ratcheting experiments carried out on piping components used in Pressurized Heavy Water Reactor (PHWR) have shown that during seismic excitation the cross section of a pipe subjected to internal pressure and cyclic bending undergoes progressive ovalization. There is, therefore, a need to understand and characterize the ratcheting behaviour in these piping steels. In this study the uniaxial cyclic deformation experiments have been carried out on SA 333 Gr 6. It is a low carbon steel used as primary heat transport piping and forged header material in PHWRs. This study is a part of an ongoing comprehensive program for characterization of the ratcheting behaviour of various piping steels used in PHWR and AHWR.

The ratcheting tests were carried out at \( \sigma_{\text{max}} = 350 \text{ MPa} \) with five different stress ratios \( R_\sigma = (\sigma_{\text{min}}/\sigma_{\text{max}}) ; R_\sigma = 0, -0.25, -0.5, -0.75, -1 \) and five levels of stress rate \( (-5 , 10 , 100, 1000, 10000 \text{ MPa/s}) \). The stress controlled tests, have been carried out by varying \( R_\sigma \). Figure shows the combinations of \( R_\sigma \) and which have shown ratcheting (represented as filled points) as well as those that have not displayed accumulation of strain (represented as open points). The trends of the stress–strain hysteresis loops have also been shown for comparison in the case of a few points in the ratcheting domain. The plot shows that at \( R_\sigma = 0 \) and \(-0.25 \) there has been no observed ratcheting. However, for the stress rates between 5–1000 MPa/s, employed for the tests at \( R_\sigma = -0.5 \) and \(-0.75 \) there has been significant ratcheting evident by the accumulation of strain. This suggests that in the present quasi-reversed tests, stress ratio has to be sufficiently negative for ratcheting to occur. Comparing the hysteresis curves in terms of the \( \sigma - \epsilon \) plots for stress ratios \( R_\sigma = -0.5 \) and \(-0.75 \), at slow and fast stress rates it has been found that at stress rate of 1000 MPa/s the hysteresis loop that develops during ratcheting is smaller than in the case of stress rate of 10 MPa/s (inset C and D in Figure). Further it has been seen from the evolution of hysteresis loops within the ratcheting domain that as the stress ratio becomes more negative the hysteresis loop opens up during ratcheting. This suggests that a negative \( R_\sigma \) ratio promotes the development of a hysteresis loop during ratcheting. The plot also shows that the accumulation of strain in the first few cycles is more rapid at slow loading conditions than at a stress rate of 100 MPa/s and 1000 MPa/s. This is more clearly seen in figure, where the effect of two stress ratios on the evolution of strain has been shown. It is clearly seen that at the slow stress rates (5 and 10 MPa/s) the strain accumulation is much faster as compared to stress rates of 100 and 1000 MPa/s. Further at these faster stress rates there is an incubation period before the ratcheting commences. The conditions observed for the two types of accumulation, one with an incubation period and one without have been shown in figure, as filled diamond and circle symbols respectively. The appearance of incubation period is also seen for \( R_\sigma = -1 \), where there is no mean stress. It is also seen from figure that at stress rate of 10000 MPa/s there was no ratcheting for both the asymmetrical and symmetrical stress cycling. The ratcheting boundary has been defined on the basis that no significant strain accumulation has been observed for \( 10^3 \) cycles.

In the present tests it has been observed that the difference in the ratcheting rates due to a change in \( R_\sigma \) from \(-0.5 \) to \(-0.75 \) increases as the applied stress rate decreases. This may be due to an interaction between stress rate and stress ratio in the slower stress rate regime where there is a possibility of rapid dislocation multiplication. At a combination of low stress rate and negative stress ratio the significant increase in strain accumulation rate may be due to dynamic Lüders band formation and larger dislocation annihilation rates. This leads to a synergistic interaction between stress rate and stress ratio, which may accelerate the onset and increase the extent of cyclic softening in the ratcheting tests.
Plot showing the domain of ratcheting observed denoted by filled symbols. The plot also shows insets for the evolution of hysteresis loops for $R_\sigma = -0.5$ & -0.75 at (A) stress rate = 100 MPa/s (B) stress rate = 10 MPa/s and the hysteresis loop obtained at $\epsilon_p \approx 0.38$ for (C) stress rate = 10 MPa/s and (D) stress rate = 1000 MPa/s.

Plot of Cumulative peak tensile strain at various stress rates for $R_\sigma$ a) –0.5 (b) –0.75

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11.10 CORROSION BEHAVIOUR OF COLD WORKED ALLOY 800 IN 673 K STEAM

Cold worked (~ 50 %) Alloy 800 containing a small volume fraction of hexagonal ε-martensite in the austenite matrix was exposed in 673 K steam of initial pH either in the nearly neutral or alkaline region for a period of 264 hours. The alloy indicated very low corrosion rates. Scanning Electron Microscope (SEM) studies of the alloy exposed in 673 K steam of initial pH in the nearly neutral region revealed a few small oxide particles whereas, a number of small oxide particles was noticed on the surface exposed in steam of initial pH in the alkaline region. Energy dispersive X-ray analyses indicated an enrichment of Fe, followed by Ni and Cr on the surfaces exposed in steam similar to bulk composition of the alloy. X-ray Photoelectron Spectroscopy (XPS) studies revealed that the surface films formed on the alloy after an exposure in 673 K steam of initial pH in the nearly neutral region contained mixed oxides of chromium, iron and nickel along with their elemental forms whereas, the presence of chromium oxide could not be detected in the surface films that formed in 673 K steam of initial pH in the alkaline region.

Hexagonal ε-martensite in cold-worked Alloy 8001

Small oxide particles in the alloy exposed in steam of initial pH 10. (A large, faceted TiN particle is visible.)

XPS spectrum recorded for (a) nickel and (b) chromium for the sample of cold worked Alloy 800 exposed in steam of initial pH 6.8.
Austenitic stainless steels are used extensively in the core of the nuclear power reactors. The main cause of failure of in-core components in light water reactors is Irradiation Assisted Stress Corrosion Cracking (IASCC) in oxygenated, high temperature (at ~ 290°C), high purity water. IASCC is the life limiting degradation mode for all the in-core components made of austenitic stainless steels and it has been attributed to the formation of a narrow but deep chromium depletion zone at the grain boundaries due to irradiation without the formation of chromium carbides. Neutron irradiation of energy higher than ~ 1 MeV in nuclear reactors results in variation of microstructure and microchemistry in austenitic stainless steels. Variation of microchemistry in austenitic stainless steels along grain boundary is termed as Radiation Induced Segregation (RIS) that results in Cr depletion at grain boundaries and segregation of Ni, S, and P. IASCC is promoted in austenitic stainless steels when a threshold fluence is reached - cracking was observed in Boiling Water Reactor (BWR) oxygenated water at a fluence above 5 x 10²⁰ n/cm² (E > 1 MeV) that corresponds to ~ 0.7 dpa (displacement per atom) for BWR and ~ 1 to 2 x 10²¹ n/cm² (E > 1 MeV) for Pressurized Water Reactor (PWR). Any enhancement of the resistance of austenitic stainless steel to RIS and IASCC will be highly useful in designing and fabricating nuclear power reactors with a long service life. This ongoing study is aimed at three main strategies for improving the resistance of austenitic stainless steels to RIS.

The first approach is to alloy the stainless steels with the dilute quantities of oversized elements such as Pt, Hf, Ce, Zr, or Nb. Austenitic stainless steels 304 and 316L with the different addition of Ce (0.01 to 0.1 wt%) have been obtained to study the effect of oversized solute addition on the RIS. The irradiation work and characterisation of chromium depletion at grain boundary as a result of irradiation by Electrochemical Potentiodynamic Reactivation (EPR) test on unalloyed stainless steel has been started. The second approach is to modify the structure at the grain boundaries (to increase the fraction of the special grain boundaries) so as to reduce the tendency for the segregation/depletion of elements at the grain boundaries. In this approach, higher fraction of special boundaries ($\Sigma < 29$) will be introduced in the material using cold rolling procedure and solution annealing. This will be subsequently subjected to proton irradiation and characterization of RIS. The characterisation of each type of grain boundary will be done using Orientation Imaging Microscopy (OIM). The third approach is to create a pre-segregation of Cr at the grain boundaries in the solution-annealed condition of austenitic stainless steels using different temperature and cooling rates during solution annealing.
In this just initiated study, accelerated irradiation using proton beam of high energy (up to 10 MeV) is used to simulate the irradiation damage due to high energy neutrons. Towards this, a high temperature experimental setup to be used for the proton irradiation at 300°C was designed and fabricated; and experiments were carried out using proton irradiation at Folded Tandem Ion Accelerator (FOTIA) and Pelletron at room temperature and at 300°C in separate experiments. Samples were irradiated to different levels of dpa and subjected to electrochemical tests after irradiation. Characterisation of irradiated samples revealed that electrochemical techniques like EPR have measured the extent of Cr depletion due to irradiation caused by different levels of irradiation damage in austenitic stainless steels. Cr depletion was not observed in the samples irradiated at room temperature up to 0.2 dpa. Cr depletion zones were noticed in the sample irradiated at 300°C up to 0.2 dpa and corresponding EPR value was 1.12. This study also confirms the fact that maximum damage is not on the surface – EPR values were found to increase up to a maximum value and then decrease with the depth from the sample surface, e.g. 1.12, 0.4 and 0.2 after repeated EPR testing and metallographic polishing. Further experiments are planned at Pelletron to evaluate the effect of the nature of grain boundary and oversize solute element addition on RIS in the austenitic stainless steels.

As received SS 304 sample with DL-EPR value of 0.05 and the sample of SS 304 irradiated at 4.2 x 10¹⁷ protons/cm² of energy 4 MeV (0.2 dpa) at FOTIA showing radiation induced segregation (RIS) and a DL-EPR value of 0.25.

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11.12 QUALIFICATION OF AUSTENITIC STAINLESS STEEL FOR 100 YEARS DESIGN LIFE OF AHWR

Austenitic Stainless Steel AISI 304LN has been selected for primary system components of AHWR. Design life of AHWR is 100 years. Low Temperature Sensitisation (LTS) has been identified as one of the material degradation mechanisms which can limit the life of component by making it susceptible to localised corrosion viz. IGC/IGSCC. Even though stainless steel may be non-sensitized to start with, welding can result in formation of chromium carbide nuclei at grain boundaries in Heat Affected Zone (HAZ) which can grow at 300°C and over long term service may result in completely sensitised microstructure. This necessitated the qualification of austenitic stainless steel material with respect to LTS susceptibility.

The Kinetics of LTS is controlled by diffusion of Cr through the
Emerging newer materials promise to be much more resistant to nitric acid environments and would stretch the limits of concentration of nitric acid that can be handled without appreciable corrosion. Fuels for newer types of reactors require use of halides in nitric acid streams. Hence, the materials of construction have to be resistant to oxidizing acids containing halides at elevated temperatures. Type 310L NAG, alloy 33 and titanium based alloys are some of the most promising alloys suitable for such environments. Many of these materials are also candidate materials for underground disposal of spent fuel. The passivity and pitting behaviour of alloy 33 has been evaluated in as received and also in welded condition in HCl solution at room temperature as well as at 650°C. The advantage of addition of 0.4% nitrogen in alloy 33 in improving the passivity and pitting resistance was brought out by comparing the results with an experimental alloy similar to alloy 33 that was prepared in the lab and did not contain nitrogen. Electrochemical corrosion testing in NaCl and HCl solutions (different concentration and pH) and immersion corrosion testing in other standard test solutions showed that alloy 33 is highly resistant to localized corrosion. Studies on welded samples showed that molybdenum rich phases do form in the heat affected zone of the weldment of alloy 33.

Initial corrosion studies on the Ti-5%Ta-1.8% Nb alloy manufactured at NFC, Hyderabad for IGCAR have shown that this alloy and its welded structure are highly resistant to corrosion in potential regions which cause transpassive corrosion for stainless steels. In addition, these were found to be much more resistant to nitric acid environments and would stretch the limits of concentration of nitric acid that can be handled without appreciable corrosion. Fuels for newer types of reactors require use of halides in nitric acid streams. Hence, the materials of construction have to be resistant to oxidizing acids containing halides at elevated temperatures. Type 310L NAG, alloy 33 and titanium based alloys are some of the most promising alloys suitable for such environments. Many of these materials are also candidate materials for underground disposal of spent fuel. The passivity and pitting behaviour of alloy 33 has been evaluated in as received and also in welded condition in HCl solution at room temperature as well as at 650°C. The advantage of addition of 0.4% nitrogen in alloy 33 in improving the passivity and pitting resistance was brought out by comparing the results with an experimental alloy similar to alloy 33 that was prepared in the lab and did not contain nitrogen. Electrochemical corrosion testing in NaCl and HCl solutions (different concentration and pH) and immersion corrosion testing in other standard test solutions showed that alloy 33 is highly resistant to localized corrosion. Studies on welded samples showed that molybdenum rich phases do form in the heat affected zone of the weldment of alloy 33.

11.13 MATERIAL DEVELOPMENT AND CORROSION MONITORING FOR SAFETY AND RELIABILITY OF REPROCESSING AND WASTE MANAGEMENT FACILITIES

The processing of spent fuel and waste and its storage form an integral part of nuclear program. The program envisages reprocessing, long term storage in metallic tanks, vitrification of high level waste and also a closed end fuel cycle. Most of these activities involve highly corrosive process fluids – nitric acids and molten glass. A lot of work is already done for materials in nitric acid environments. The mechanism of corrosion resistance of the Nitric Acid Grade (NAG) of type 304L has been studied in detail. The strict control on chemical composition, especially on carbon, nickel, chromium, silicon and phosphorus together with controlled microstructure (fine grain size and retained cold work) helped improve resistance to intergranular corrosion and resistance to general corrosion in concentrated nitric acid solutions. The lower general corrosion rates in nitric acid (5 -10 mpy) allow longer life of stainless steel components as the oxidizing higher valence ions that enter the process fluids as (general) corrosion products increase the corrosiveness of the process fluid with time. This is especially beneficial in applications where once flow conditions do not exist e.g. in acidic waste storage tanks.

The role of inclusions in corrosion of stainless steels in nitric acid environment has been brought out clearly in our earlier study. The role of type of inclusions (oxides/nitrides/sulfides/silicates etc) on initiation of corrosion in nitric acid medium will be studied separately. Recent work on the mechanism of end grain pitting has shown that processing of the stainless steels may also result in chromium depletion along the flow lines in highly worked products e.g. tubular products. EPMA analysis had shown the presence of chromium depletion in regions adjacent to the flow bands and the end grain corrosion attack was along the direction of these flow bands. Earlier this type of segregation of Nb/Ti along flow bands and end grain corrosion was reported for stabilized stainless steels.

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highly resistant to end grain corrosion also. The general corrosion rate was very low, < 2 mpy in concentrated boiling nitric acid solutions (e.g. practice C, A 262, ASTM). The influence of beta phase that gets precipitated during welding/processing was not found to be harmful possibly because of absence of depletion of the alloying elements around the beta phase.

Comparison of the localized corrosion behaviour of alloy 33 in mill annealed condition and welded condition with that of alloy 22 in 1 N HCl solution at 65°C

Vitrification of high level liquid waste involves molten glass and the materials of construction have to be resistant to degradation in it for a sufficiently long timeframe. The interaction of materials of the process pot (alloy 690) with molten glass needs to be studied in detail and mechanism of degradation established. It is of utmost importance to be able to predict the “safe” operating regimes in terms of temperature and time for the process pots used in the vitrification process.

In future, different materials, including alloy 690 and its variants will be exposed in molten glass at defined temperatures between 900 to 1200°C for different time durations. This would help in choosing the most optimum material and also to schedule replacement of components ahead of its anticipated operation life to ensure safe and reliable operation. Other factors like concentration of acidic waste stream during vitrification and use of other corrosive additives will be accounted for to arrive at a safe material-process combination for a specified duration.

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