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Radiation Damage of Structural Materials

for Fast Reactor Fuel Assembly (3)

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RADIATION DAMAGE OF STRUCTURAL MATERIALS FOR

FAST REACTOR FUEL ASSEMBLY

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PRINCIPLES OF DESIGN OF RADIATION RESISTANT MATERIALS FOR FAST REACTOR FUEL ASSEMBLY

The present chapter consists of three parts: (1) the basic principles of design of void swelling resistant materials for fast reactor fuel assembly (2) Development of cladding materials for present fast reactors and (3) Ferritic steels for future fast reactors.

HISTORICAL PERSPECTIVE:

It would be surprising today to learn that the first “canning” material used in Fermi’s first reactor was an aluminium alloy !!! With impetus provided by atoms for peace movement, considerable efforts were spent in early 60’s to increase the burn-up of the fuel. A large number of fuels with an attempt to increase the fission cross-sections were attempted. Only in late 60’s, it was realized that the burn up of the fuel was limited more by the “cladding” material and not by the fuel *per se.* This discovery was accidentally made by Cowthorne in his paper in Nature in late 60’s. Immediately, nearly four governments launched massive programmes in various names, like National Cladding and Duct Development programme in USA.

High temperature being one of the concerns, nickel based super alloys of those days and austenitic stainless steels were the target materials for development. UK took the lead in developing the nickel based super alloys. Soon, the realization of helium embrittlement focused further attention only to austenitic stainless steel. Prior to 1974, cold worked austenitic stainless steels received the major thrust. However, testing this in EBR II showed unacceptable high swelling for use in FFTF. Till about 1986, variants of austenitic stainless steel were attempted, one of which is D9, whose performance in

Superphenix was satisfactory up to 100 dpa of burn up or fluence. Further improvements were achieved by minor alloying elements modification.

Parallelly, the fossil industry was developing high temperature materials for increased thermal efficiency at high temperature and high pressure in fossil power industry. HT 9, a ferritic alloy based on 12% chromium, marketed by Sandvik was accidentally found to have nearly zero void swelling, even up to about 180 dpa. Following this clue, a large number of ferritic alloys have been developed for the nuclear core and extensive literature is available demonstrating their advantages and their limitations. Presently, the target is to increase the burn up to about 200 dpa with 100 years as lifetime and an operating temperature of about 700 C !!! a rather tall order for the metallurgists and material scientists.

PRINCIPLES OF DESIGN OF RADIATION RESISTANT ALLOYS:

The principles to be discussed below were learnt from the painstaking efforts of material scientists over nearly five decades, initially by experiments with accelerators which UK pioneered, followed by reactor experiments, along with extensive modeling studies. However, designing an alloy truly guided by the principles of materials behaviour is not yet achieved.

It is clear from chapters.1 and 2 that the microstructure of the material governs the void swelling behaviour. In order to view the subject from basic point of view, it is helpful to classify the fast reactor core materials into two major groups: the austenitics and the ferritics. This is required since the radiation damage events depends very much on the structure of the basic lattice and the interactions of the solute atoms with the defects generated during irradiation.

Austenitic Stainless Steels:

These steels anchor around various combinations of iron, nickel, chromium, molybdenum and carbon, with the requirement that the fcc austenite phase is stable at room temperature. This is known to possess excellent high temperature mechanical properties, in the absence of irradiation.

The effect of Ni content in Fe matrix on swelling was studied systematically. It is found that addition of nickel to iron lattice is beneficial in increasing the incubation dose up to about 50% nickel, while no change is observed in the steady state swelling rate. This is understood in terms of high binding energy (0.26 eV) of nickel with vacancies.

Chromium in amounts more than 12%, is added to ensure corrosion resistance to the steels and referred to as 'stainless steel'. However, addition of chromium beyond 15 % is not beneficial for swelling. The deleterious influence of chromium in void swelling can also be understood in terms of low binding energy between chromium atoms and vacancies, 0.06 eV. Swelling increases monotonically with addition of chromium in the range 15-30 %, reaching a maximum at around 15 % chromium. Swelling in ferritic alloys of course is not a problem, but is maximum with 15 % chromium. Figure.3.1. shows the combined effect of nickel and chromium concentration in the swelling.

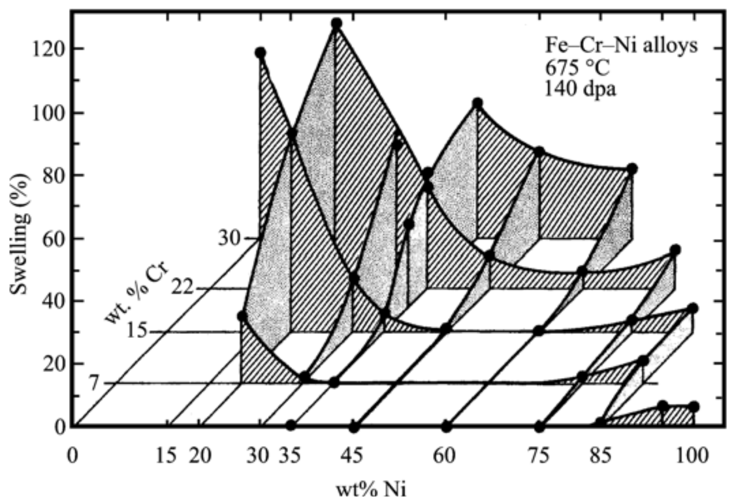


Figure.3.1. Effect of concentration of nickel and chromium on swelling. Increase in nickel up to 50 % reduces swelling, by increasing the threshold dose and not altering the swelling rate. Chromium increases the swelling, maximum being around 15 %.

Effect of Minor Elements:

Addition of minor elements that bind strongly with vacancies and interstitials is beneficial to suppress void swelling. These elements are useful to reduce effective mobility, thus preventing defects from reaching sinks and promote the following recombination reaction: V + I --→ lattice atom and annihilate the point defects.

Oversized elements like hafnium also imparts beneficial effect in reducing swelling. Ti, P, Si and B have beneficial effect mainly by virtue of high binding energy with point defects. Each of these elements are briefly discussed with respect to their positive role:

<u>Titanium:</u> The binding energy of titanium with vacancies is very high, 0.3 eV. Hence it strongly binds with the vacancies in the lattice, reducing the supersaturation of free vacancies, which lowers the swelling rate. Hence, it is always beneficial to retain a certain amount of titanium in the solid solution to reduce swelling. The effect of titanium is maximum when silicon and phosphorous also is present in the matrix.

<u>Phosphorous</u> is the next important beneficial element in austenitic stainless steel. This has the same effect as titanium. In addition, the diffusion or the mobility of P-Vacancy complexes are also very high, thus promoting the recombination rates, which enables suppression of swelling. Thus, phosphorous, reduces swelling in two ways: at low temperatures, phosphorous- defect complex interactions, reduce vacancy supersaturation

and increase recombination, finally leading to low swelling; at high temperatures, precipitation of phosphides enhance the annihilation rate of point defect fluxes and reduce swelling, which will be explained later.

Silicon has same effects as that of phosphorous, w.r.t. binding vacancies reducing supersaturation and lowering the swelling. The diffusion or the mobility of silicon-vacancy complexes are far higher than other solutes in austenitic steels, thus contributing to lower swelling by increasing the recombination rates.

Boron plays a positive role, in suppressing swelling in a different manner: Boron reduces the mobility of carbon and nitrogen by combining with them and reduces rate of formation of carbides and carbo-nitrides. This enables the solid solution to retain beneficial elements like Ni, Mo, Si, Nb to be retained.

The major lessons learnt during the studies on effect of solute elements in austentic steels are the following:

Add oversized elements with high binding energy with point defects and if possible, maximize the mobility of the complexes formed between the element and the point defects to enhance the recombination rates and hence reduce swelling rates.

Influence of Second Phase Particles:

When certain second phase particles are distributed in the lattice of austentic stainless steels, void swelling is reduced by two mechanisms:

(1) Interfaces between precipitates and matrix act as recombination sites for annihilation of vacancies and interstitials, thus reducing swelling;

(2) Inhibit dislocations climb necessary for dislocations to act as preferential sinks for interstitials and retard void growth.

However, most of the precipitates act as sites for nucleation and growth of voids, since they act as collector for vacancies. The difference lies in the nature of the interface between precipitates and interface. If there are coherent precipitates, they offer the best site for constrained recombination of defects, while incoherent precipitates serve as sites for collection of defects, like grain boundaries, which are channeled into voids.

There are two major classes of precipitates in austenite matrix: those which suppress swelling due to enhanced point defect recombination at the particle/matrix interface, like MC (TiC, NbC or VC), Fe_2P or Ni_3Ti; those M_6C- $(Cr,Mo,Ni)_6C$ or $Ti,Ni)_6C$ or G-phases $(Ti,V,Nb,Mn)_6(Ni,C0)_{16}$ Si_7 and γ'(Ni_3Si, Ni_3Ti), which enhance swelling by depleting the austenite of beneficial elements like Ni, Si, Ti, P, This effect is called the 'solid solution decay'.

Another factor is the preferential bias of undersized and oversized precipitates offer to point defects in the austenite matrix. Incorporation of large number density of coherent, stable, fine TiC introduces interfaces which trap less mobile vacancies, offering higher recombination probability with the fast moving interstitials. Hence, the vacancy supersaturation is reduced and consequently the void swelling. This is the basic principle of design of D9, basically an austenitic stainless steel with 15% Cr, 15% Ni and Ti and C in fixed ratio to achieve desirable number of TiC coherent precipitate. It should be ensured that enough Ti is also left in the matrix, which by itself binds with vacancies to reduce swelling, as explained earlier. Figure.2. shows the high resolution image of TiC in austenite matrix. This modification in the design of austenite introduced considerable increase in the threshold dose form 30-40 dpa for cold worked 316 austenitic steels to 80 dpa for austenitic stainless steel.

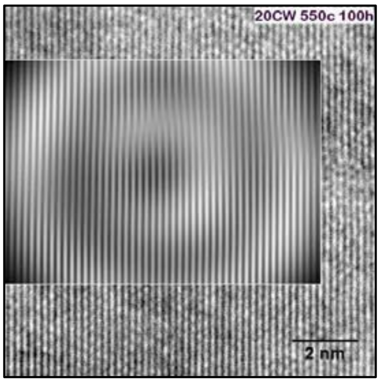


Figure.2. High resolution electron micrograph of TiC in an austenite matrix in D9. The inset shows the filtered image of lattice planes.

Another design principle in the development of austenitic steels is to identify the benefit of trapping vacancies with oversized precipitates like TiC and interstitials with undersized precipitates like Fe_3P by adjusting the concentration of minor elements, i.e., phosphorous. Figure 3 shows the formation of needle like phosphides in D9 with adjustment of minor elements, along with the corresponding change in the threshold dose.

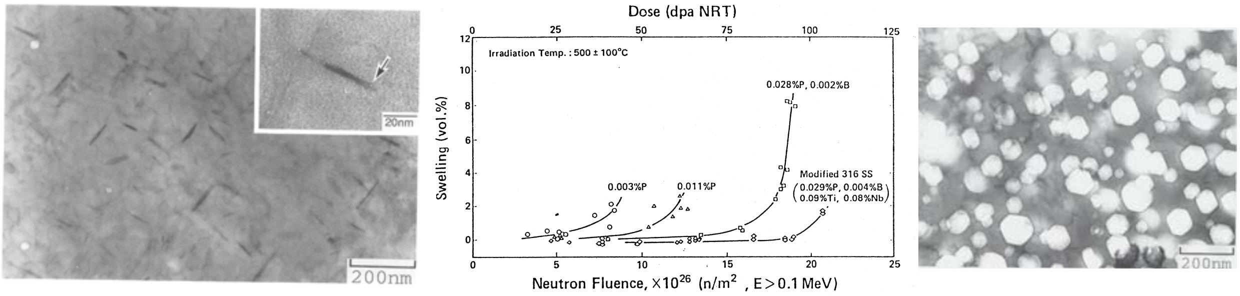


Figure.3. TEM image of fine coherent iron phosphides at 800 K after 43 dpa. These fine precipitates delay threshold dose, as seen in (b). The dissolution of phosphides leading to copious precipitation of voids at 85 dpa is seen in (c).

These phosphides have additional advantage of trapping helium bubble and thus reducing void swelling.

The present approach to design of void swelling resistant austenitic stainless steels is to optimize the composition of the minor elements in 15%Cr-15T %Ni steels, in such a way that combination of oversized TiC (trap vacancies) and undersized Fe3P (trap interstitials), maximizes the threshold dose beyond 100 dpa.

Ferritic Steels:

It has been stated that the void swelling depends crucially on the structure of the matrix lattice in which irradiation produces the excess defects. Though it was accidentally found that the ferritic steels, which have far inferior high temperature mechanical properties than austenitic stainless steels displayed excellent radiation resistance, nearly twice better. The threshold dose for swelling was as high as nearly 200 dpa. This has encouraged the development of ferritic steels for core component application for a fast reactor fuel assembly.

Why ferritics show superior swelling resistance compared to austenitics ? Extensive basic studies on ferritics identified the following reasons as the origin of superior swelling resistance in ferritic steels:

(1) The relaxation volume for interstitials, *i.e.,* the volume of the matrix in which distortion is introduced by creating an interstitial, in bcc ferrite is larger than fcc austenite. For every interstitial introduced, the lattice distortion is high and hence the strain energy of the lattice. Hence, the bias towards attracting or accommodating interstitials in the bcc lattice is less. This leaves higher density of 'free' interstitials in the bcc lattice than fcc lattice. As a result, recombination probability with vacancies increase significantly and supersaturation of vacancy reduces. Consequently, the void nucleation and swelling is less.

(2) The migration energy of vacancies in bcc iron is only 0.55 eV, against a high value in fcc austenite, 1.4 eV. Vacancies are more mobile in bcc than fcc,

increasing the recombination probabilities in bcc ferrite. Another factor is the high binding energy between carbon and vacancy in bcc iron (0.85 eV), while it is only 0.36 to 0.41 eV in austenite. This leads to enhanced point defect recombination in bcc than fcc, due to more trapping of vacancies by carbon or nitrogen.

(3) In bcc iron, it is known that there is a strong interaction between dislocations and interstitials solutes, forming atmospheres of solutes around dislocations. This reduces the dislocation bias for interstitial capture and also inhibit dislocation climb. Hence, dislocations remain as unsaturable sinks for excess interstitials.

These fundamental differences in the behaviour of solutes and point defects in bcc lattice make ferritic steel far superior to austenitic steels, with respect to radiation damage.

The challenging task for materials scientists to use ferritic steels directly in fast reactor fuel assembly was with respect to enhance the high temperature mechanical properties of the ferritic steels, especially high temperature creep life, irradiation creep and irradiation embrittlement. While attempts were diverted to develop ferritic steels as core component materials, some more engineering problems with respect to materials technology of joining these steels, namely Type IV cracking in their weldments was also identified. Since these are system specific problems, they will be discussed in section 3 of the chapter, where development of ferritic alloys for fast reactor core is discussed. The minimization of embrittlement and the overcoming of Type IV problems could be carried out by optimizing the chemistry of the steel, especially the chromium content, leading to many commercial steels, mainly revolving around 9 % to 12 % chromium, where the embrittlement is the least.

In recent years, an attempt to increase the high temperature creep life of ferritics has led to a new concept of strengthening the steel using 5nm particles of yttria, leading to the oxide dispersion strengthened ferritic steels. These steels, if proved to be as good as austenitic stainless steels at high temperature, the limit of temperature could be reached to about 600, despite using ferritic steels. This would enable us to achieve both void swelling resistance upto a burn up of about 200 dpa and reach temperature of around 600 C. Figure.4. summarises the performance of the three generations of materials developed with respect to the irradiation dose and high temperatures that can be achieved.

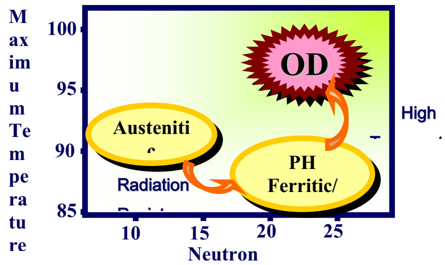


Figure.4. The maximum temperature limits and the radiation resistance of the three generations of core component of materials for fast reactors: Austenitic stainless steels are excellent for high temperatures up to 700 C and dose upto 80 to 100 dpa. Ferritic steels display radiation resistance up to about 200 dpa, but the temperature capability is reduced to about 550C. The oxide dispersion ferritic steels, which are being developed, are promising materials for combining radiation resistance of ferritic steels and achieve better high temperature properties.

When a material for a component is developed for actual use, it is necessary to identify the life limiting factors. For instance, in core component materials, the swelling resistance and irradiation creep are important. However, it is necessary to evaluate the material from all aspects, in-reactor performance, materials technology and postirradiation disposal. Hence, the second and third part of this chapter deals with discussion of all aspects of austenitic and ferritic steels, without confining to only radiation resistance. These are based on the following two papers: *Development of Cladding Materials for Sodium-cooled Fast Reactors in India by Baldev Raj, Divakar Ramachandran and M. Vijayalakshmi, Indira Gandhi Centre for Atomic Research, Kalpakkam, TN 603102, INDIA, in Transactions of Indian Institute of Metals, 2009* and *Embrittlement Problem in 9Cr-1Mo Ferritic Steel and its weldment - Methods to Overcome, Baldev Raj, S. Saroja, K. Laha, T. Karthikeyan, M. Vijayalakshmi and K.Bhanu Sankara Rao in Journal of Materials Science, 2009.*

Development of Austenitic Steels: D9 and beyond

The material of choice for clad of fast reactors is a titanium modified SS316, also known as Alloy D9 (15%Cr-15%Ni-0.2%Ti), in the 20% cold-worked condition. Austenitic stainless steels are favoured for fuel pin cladding and other core component applications, since they possess the required strength characteristics up to 923 K. Early studies on creep properties of alloys with titanium to carbon ratio between 4 and 6 showed that titanium content strongly influences the creep rupture life. Alloys with Ti/C ~ 4 showed the best creep rupture life at 973 K. However, the rupture ductility was found to be poor. On the basis of metallographic analysis of the samples it was suggested that this is due to the intragranular precipitation of titanium carbides in the cold-worked matrix that led to the formation of creep cracks. Thus, it was recognised that the propensity for carbide formation needed control and it was recommended that the composition be optimised such that the Ti/C ratio was limited to ~ 4. However, the limiting factor at moderate reactor operating temperatures of up to ~ 873 K is void swelling which ultimately limits life of the fuel pin leading to a reduced burn-up of about 100 GWd/tonne. Hence, for clad tubes of the fuel pins the driving force for development of new structural alloys has been the required improvement in void swelling resistance. Based on mechanical characterisation, two prospective austenitic stainless steels with compositions differing in Ti content have been selected for evaluation of void swelling resistance.

Ion-irradiation with 5 MeV Ni^{2+} ions after prior He implantation to mimic fast reactor conditions has been adopted to evaluate radiation damage in these compositions. TRIM calculations have been used to determine the fluence and irradiation time required to produce ~ 100 dpa as the damage peak for the 5 MeV Ni^{2+} ions in stainless steels. The degree of void swelling resulting from the irradiation is measured in terms of the step height between masked and unmasked regions of a 5 mm x 12 mm sample surface. Damage rates ~ 7 x 10^{-3} dpa/s could be achieved with a 1.7 MV Tandetron accelerator. Figure 5 shows the results of such irradiation experiments on two candidate alloys with Ti/C ratios of ~ 6 and ~ 4 in 20% cold-worked state, irradiated with 5 MeV Ni^{2+} ions after He implantation to a concentration amounting to ~ 30 appm, in the temperature range 723 – 973 K. It is seen that the alloy with the Ti/C ~ 6 (Ti ~ 0.25 wt%) exhibits significantly lower swelling of ~ 4% compared to nearly 15% for the alloy with Ti/C ~ 4 (Ti~ 0.15 wt%).

The peak swelling temperature is also significantly lower at 823 K for the former alloy, 100 degrees lower than the corresponding temperature for the latter alloy. Based on the temperature shift estimation to allow for the much smaller damage rate in a fast reactor, the peak swelling temperatures for Alloy D9 with Ti/C ratios of 4 and 6 are estimated to be 649 K and 598 K respectively.

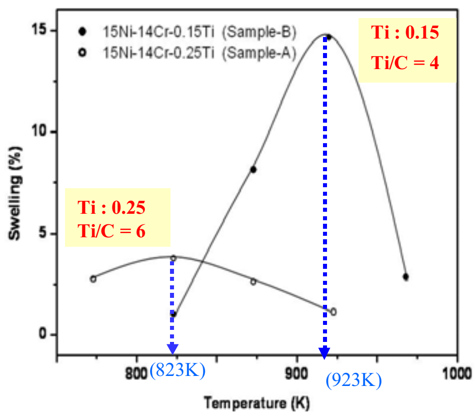


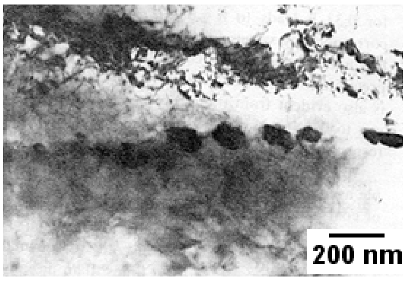
Figure.5. Void swelling behaviour of Alloy D9 with (a) 0.25 wt% Ti, and (b) 0.15 wt% Ti

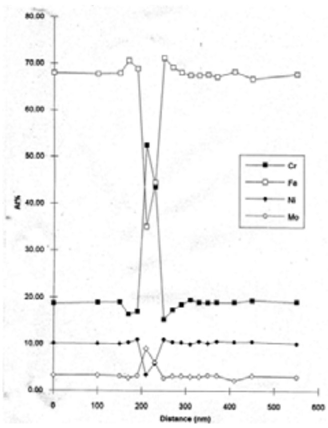
The main influence of titanium in this alloy is through uniform distribution of fine secondary precipitates of TiC stabilising the cold-worked dislocation structure. The fine precipitates have a high degree of lattice mismatch with the austenite matrix and the interfacial defects that result can be monitored using a technique such as positron annihilation spectroscopy. The positron life-times were measured as a function of the isochronal annealing temperatures for the above two alloys. The results are interpreted as showing a higher number density of TiC precipitates and a lower temperature of onset of precipitation in the alloy with a higher Ti content. Thus the reduced swelling in this alloy can be correlated to a higher number density of fine TiC precipitates that trap voids at the matrix – precipitate interface, while the lower peak swelling temperature is attributed to the effect of titanium in solid-solution on the effective diffusion coefficient of vacancies in the austenite lattice.

Minor elements such as Si, Ti and P have a major influence on the void swelling behaviour of Alloy D9. In an effort to further optimise the alloy composition around the nominal Alloy D9 levels and identify an improved alloy D9, a series of alloys were produced by varying the concentrations of Ti, Si and P around their nominal values in standard Alloy D9. As a result of ion irradiation studies on these alloys, an optimised austenitic steel based on 15Cr-15Ni-Ti (Alloy D9) with Si, and P additions ("InD9") are proposed for fuel pin cladding applications. The InD9 alloy with optimum composition of minor elements is expected to allow safe operation up to ~ 150 dpa for fuel clad material.

Grain boundary optimisation through thermo-mechanical treatments

Sensitisation is one of the major problems in austenitic stainless steels, and their weldments leading to profuse cracking. This is known to occur in austenitic stainless steels as a result of precipitation of Cr-rich carbides at grain boundaries (Figure.6a) which leads to a Cr-depleted zone near grain boundaries (Figure.6b), eventually leading to intergranular corrosion related material failures. The availability of a technique to determine statistically significant grain boundary character distribution over a large umber of grains has enabled derivation of a number of parameters that can be correlated to materials properties. Such correlations are essential for establishing a scientific basis to materials development. One such example in the materials development for fast reactors is the determination of effective grain boundary energy (EGBE) and its correlation to sensitisation of AISI 316L(N) stainless steels. The time to sensitisation generally reduces with cold-work up to a level of 15%, and increases with a decrease in carbon and increase in nitrogen in the steel. It has been known for some time that corrosion behaviour can also be influenced by grain boundary character, which in turn can be modified through a tailoring of the thermo-mechanical treatments. However, until fairly recently, this was essentially an empirical observation that was applied without a detailed understanding of the basis. The difficulty was in defining a single measurable parameter that could represent the averaged state of grain boundary character in a sample. Developments in electron back-scattered diffraction (EBSD) has enabled the rapid determination of grain boundary character for a large number of grain boundaries in a reasonable time scale. However, it is recognised that the grain boundary character determines the grain boundary energy, which in turn plays a role in interfacial reactions including grain boundary precipitation. It is necessary to define a quantity that describes the overall state of grain boundary energy in a material to correlate the results of an EBSD investigation with a macroscopically observed effect such as sensitisation. EGBE is defined as $\dfrac{\sum_i f_i \gamma_i \left(\dfrac{\Delta\theta_i}{\theta_{\max}}\right)\dfrac{4}{d}}{\gamma_{\max}}$, where $\gamma_i = \left(1 - \dfrac{1}{\sqrt{\Sigma_i}}\right)\gamma_{\max}$ is the energy of grain boundary of class i with a CSL notation Σ_i, f_i is the fraction of such boundaries, $\Delta\theta_i$ is the average deviation from exact CSL configuration, θ_{max} is the maximum deviation allowed for that boundary, d is the grain size and γ_{max} is the energy of random boundaries. It can be determined using f_i and $\Delta\theta_i$ derived from an EBSD experiment. It is possible to increase the percentage of coincidence site lattice (CSL) boundaries up to 70% by controlled thermo-mechanical treatments. For a material that has a large fraction of grain boundaries with CSL misorientations, the EGBE has low values while a material with maximum randomised grains will have a high EGBE. It was possible to alter or delay sensitisation by an appropriate thermomechanical treatment. The degree of sensitisation (DOS) and the EGBE has been determined in AISI 316L(N) as a function of thermal treatments. As seen from Figure.6c, at low as well as very high effective grain boundary energies, the susceptibility to sensitisation is greatly reduced. These states correspond to large fractions of grain boundaries being of low energy CSL type or very high angle grain boundaries. A number of thermomechanical treatments can be designed to achieve particularly low effective grain boundary energies for the material. It is found that there can be a ten-fold increase in the time to initiate sensitisation by suitably engineering the grain boundary state in a material. This is of high importance in practical welding situations commonly encountered during fabrication or repair of nuclear reactor components.





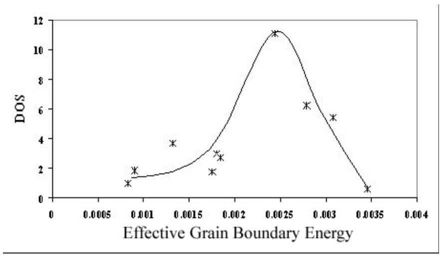


Figure.6. *(a) Formation of Cr-rich carbides near the grain boundary in a AISI 316 stainless steel in a 5% cold-worked state after treatment at 1073 K for 15 minutes, (b) energy dispersive X-ray spectroscopy (EDXS) results from the sample in (a) showing the degree of Cr depletion at the grain boundary, (c) Degree of sensitisation as a function of the effective grain boundary energy (EGBE) in an AISI 316LN stainless steel showing particularly low values for low energies (CSL boundaries) and high energies (random boundaries). EGBE is normalised to γ_{max} and hence is represented as a dimensionless quantity.*

Modelling in prediction of Materials Performance:

Modelling lies at the core of any materials engineering project. The ability to model a given material property or process enables innovative solutions to engineering problems that saves a lot of experimentation time. Many times development of reliable and robust models is essential to predict material behaviour for domains where experiments cannot be performed, for example, for time scales ~ 60 years. In this section, we describe a specific case studies in welding of austenitic steels, where a novel neural network model has been adapted to predict ferrite number. Welding being an important on-site fabrication technique used in the construction of nuclear reactors, such studies are of immense importance in ensuring that materials technology designed in laboratory clean environments is translated into sound structural components at the construction site.

Bayesian neural network model for ferrite number prediction in SS welds

A minimum ferrite content is necessary to ensure hot cracking resistance in austenitic stainless steel welds, while an upper limit on the ferrite content is essential to avoid sigma phase embrittlement. The ferrite content results from the microstructural evolution during the welding process. Traditional models of ferrite content, quantified as Ferrite Number (FN) use linear expressions in terms of Cr-equivalent and Ni-equivalent concentrations. This has been found to be inadequate to represent the complex relationship between composition and FN since inter-solute interactions are ignored. In this context, an accurate Artificial Neural Network (ANN) based predictive model that accounts for the effect of the various alloying elements has been developed. The Bayesian neural network models were employed to relate thirteen compositional variables to a single FN output. For this about half of 1020 datasets were used to train the network and the remaining half used to test performance of the network. Using this mode, it was possible to establish varying non-linear contributions of individual elements to FN depending on the base composition.

Another important consideration in austenitic stainless steel welding is the solidification mode. The weld metal composition has to be tailored to promote formation of ferrite within a safe window, for minimising solidification cracking susceptibility and to reduce the amount of slag formation. Bayesian classification neural network has been applied to classify solidification modes based on composition. Based on this model, it is shown that Ni, Cr, Mn and N are the main elements whose concentrations influence the solidification mode. The model has achieved a predictive accuracy better than 81% on an independent dataset. This degree of reliability of the prediction of solidification mode, given an alloy composition is of great practical significance. Correspondingly, with close control of Ni, Cr, Mn and N it is possible to obtain primary ferritic solidification mode and hence reduce the propensity for cracking during solidification and eliminate the slag produced by arc welding.

Ferritic Steels:

Rapid strides have been made the world over in the design and development of advanced ferritic martensitic steels by modification of chemistry and processing methods. The high chromium 9-12% ferritic martensitic steels are being developed with continuous improvements in performance by optimization of carbon content, addition of solid solution strengtheners Mo and W, carbide forming elements Nb and V, partial substitution of Mo by W and controlled addition of elements like N (0.03 – 0.05 wt %) and B for enhanced creep strength and stability of microstructure. Commercial steels like T91, T92, HT9, E911 and HCM12A show very high creep rupture strength and are proven materials for high temperature applications. The new Cr-Mo-W steels are 'code approved' for thick section applications for operations up to 893K. Presently, modified 9Cr-1Mo steels in which V and Nb contents have been optimized, are being used throughout the world for super heater tubings, headers and pipings of conventional as well as nuclear power plants with steam temperatures up to 866 K.

The ferritic steels, which basically have developed out of the conventional creep resistant steels, called low alloy steels, have been developed for lowering DBTT and better irradiation creep at high temperatures. Of all the materials developed, ferritic steels show the best void swelling resistance. The threshold dose is as high as 160 dpa as shown in figure.7.

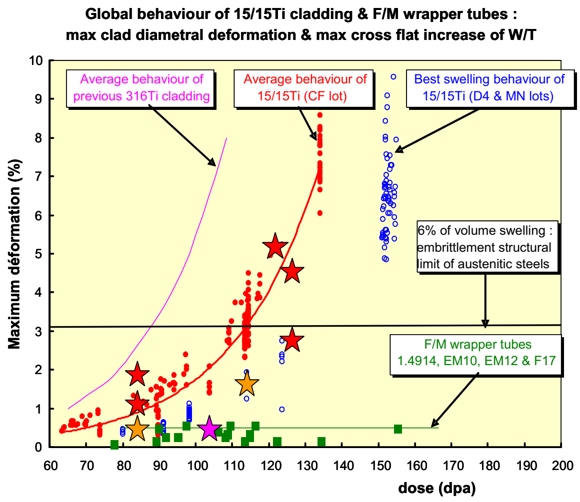


Figure.7. Void swelling vs dose for different engineering materials.

Extensive evaluation of the embrittlement behaviour of the ferritic steels for different chemistry is shown in figure 8. The merit in focusing on chemistry around 9 % chromium is very clear based on the observation of minimum shift in DBTT around this composition, under irradiation.

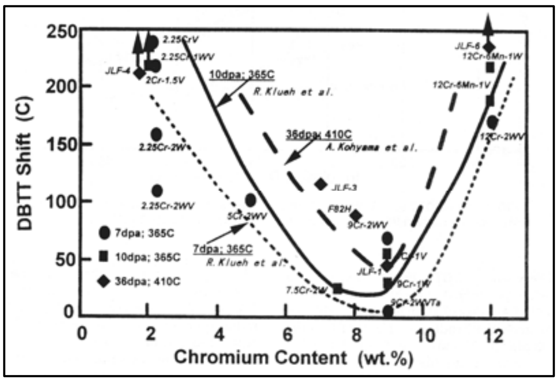


Figure.8. Variation of DBTT shift under irradiation with chromium content in ferritic steels.

Addition of phosphorous, copper, vanadium, aluminium and silicon are known t increase DBTT while sulphur reduces the upper shelf energy. The choice therefore is basically around the 9 to 12 % chromium steels in various countries.

Development of Oxide Dispersion Strengthened Ferritic Steels:

The high temperature capability is reduced to 550 C with the above ferritic steels. Hence, oxide dispersion strengthened steels were developed, to achieve the maximum swelling resistance without compromising the high temperature capability, which is yet to be commercialised.

The design of oxide dispersion strengthened steels, ODS steels for FBR clad applications is based on Fe-Cr-W-Ti-Y2O3, either the martensitic 9Cr or the ferritic 12 Cr steels.The dispersoids which confer the high temperature creep life to the ferrite matrix are expected to be in the size range of around 5 nm with a volume fraction around 0.3 %. The yttria dissolves in it some amount of titanium, leading to the formation of mixed, complex oxide , namely TiO2.Y2O3. The processing route worldwide is the powder metallurgy route of mechanically alloying pre-alloyed powders of Fe-Cr-W-Ti-C + T2O3, followed by hot extrusion and rolling or hipping with final heat treatments. The improvement in high temperature mechanical properties is achieved by the uniform distribution of stable fine oxide particles, as shown in figure.9.

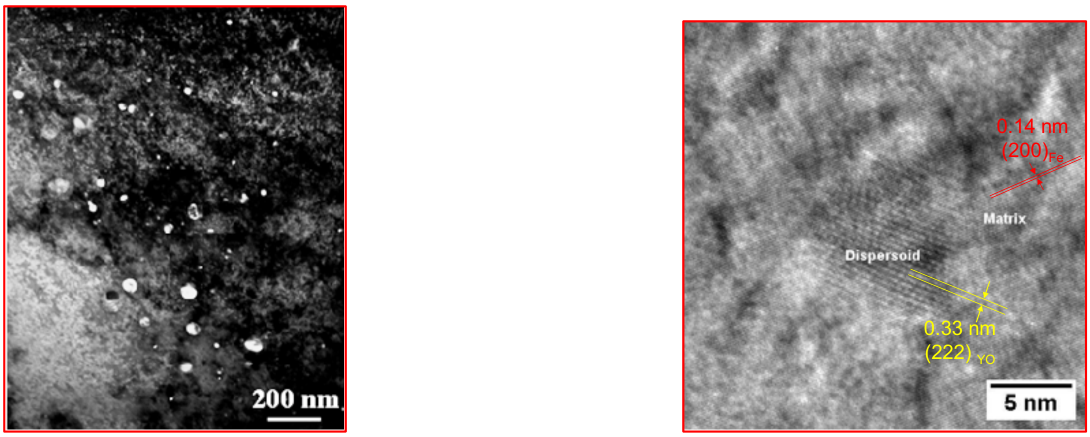


Figure. 9. Transmission electron micrograph of dispersion of 5 nm oxide particles in ODS steels, being developed for future fast reactors.

The improvement in the high temperature creep properties and embrittlement behaviour is shown in figure.10.

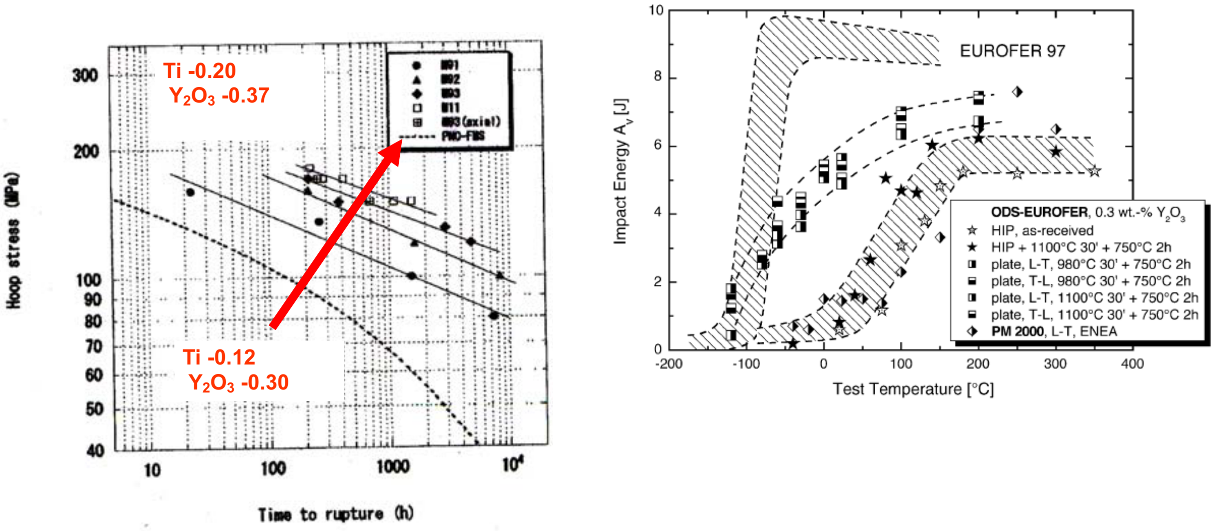


Figure.10. High temperature creep behaviour and (b) embrittlement behaviour of ODS steels, compared with other options in the same family of steels.

However, the anisotropy observed in steels with chromium more than 12%, less oxidation resistance in chromium ~9 %, irradiation behaviour of the new ODS steel, the stability of the fine oxides under irradiation are under investigation before commercial utilization.

Methods to Overcome limitations of ferritic steels:

The steel in the normalized and tempered condition has a tempered martensitic structure with a preponderance of monocarbides that impart the necessary creep strength, while the prior austenite grain and lath boundaries are decorated with Cr rich $M_{23}C_6$ precipitates which increase the thermal stability of the steel. It is reported that thermal aging at temperatures above 773 K causes gradual but continuous degradation in upper shelf properties in addition to increase in the Ductile to Brittle Transition Temperature. It is also well established that the fracture toughness of many power plant steels deteriorate during service at elevated temperatures. These changes are due to two main reasons namely segregation of tramp elements to prior austenite grain boundaries which make the grain boundaries de-cohesive; and evolution of carbides and intermetallic phases (Figure.11), which. cause progressive changes in the tempered martensitic microstructure and are prominent factors that deteriorate the fracture properties of the steel.

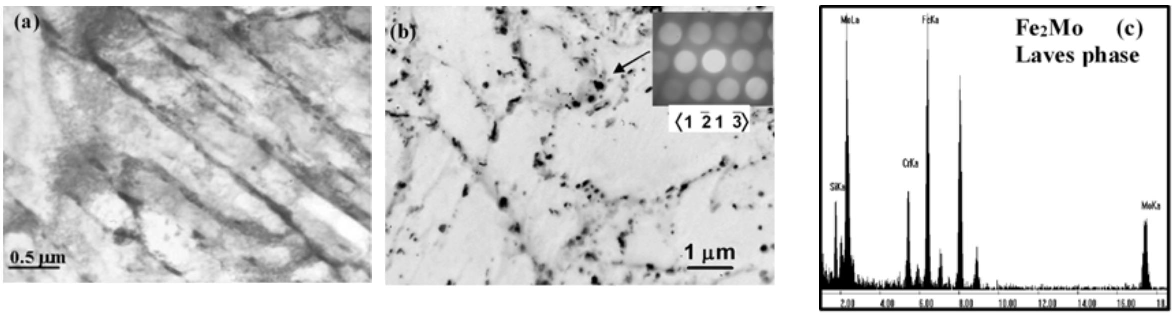


Figure.11. TEM micrograph showing (a) retention of lath structure after aging for 5,000h at 773K (b) from a carbon extraction replica showing the distribution of inter and intralath precipitates; inset shows the diffraction pattern from the arrow marked precipitate identified as Fe_2Mo Laves phase along $<1\ \bar{2}\ 1\ \bar{3}>$ zone axis and (b) EDS spectrum showing Fe and Mo nature of Laves phase, responsible for the loss of ductility.

The 9-12%Cr steels perform well under irradiation in terms of void swelling, thermal and irradiation creep and fatigue properties compared to their austenitic counter parts, which are materials issues crucial in achieving high burn-up in fast reactors. Presently, the 9-12%Cr steels are promising for high temperature applications such as clad and wrapper of fast reactors. Although the 9-12% Cr-Mo steels have several attributes favoring them for core components there are several challenges that need to be addressed.

The major challenges are the reduced creep strength at temperatures higher than 823K and reduction in toughness on irradiation to high displacement doses. For body centred cubic materials such as ferritic martensitic steels, radiation hardening at low temperatures (< $0.3T_M$) can lead to a large increase in the ductile to brittle transition temperature and lowering of impact energy even for low radiation dose such as 1dpa (displacement per atom). The minimum operating temperature to avoid embrittlement in ferritic martensitic (F/M) steels is ~ 473-523 K, while the upper limit is controlled by four different mechanisms: thermal creep, high temperature helium embrittlement, void swelling and compatibility with fuel and coolant. Void swelling is not expected to be significant in F/M steels up to damage levels of about 200dpa. The 12Cr steels, HT9, show a large shift (125K) in DBTT as compared to modified 9Cr-1Mo steel (~54K).

An approach to reduce shift in DBTT is a major issue in ferritic steels for core component applications and efforts to overcome this problem by selection of high purity metals, adoption of double or triple vacuum melting for steel making, strict control of tramp and volatile elements and development of special processing methods, which would improve the nature of grain boundaries (grain boundary engineering) are in progress. The nature of embrittlement varies for different components of the reactor. For removable components such as clad, which are subjected to high temperature and pressure, with a residence time of a few years, creep embrittlement is the issue which decides their design and performance, while for permanent support structures increase in hardening and loss in fracture toughness on irradiation are major issues.

The 9Cr-1MoVNb steel derives its creep strength from the solid solution strengthening, dislocation substructure strengthening and precipitation strengthening.

Molybdenum mostly confers solid solution strengthening to the steel. The creep strength of the alloy is significantly higher than the 2.25Cr-1Mo and plain 9Cr-1Mo steel for longer test durations, until about 873K and is almost comparable to type 304 austenitic stainless steel**.** However, the weld joints have always been areas of concern due to the heterogeneous microstructure, which is described below.

Microstructural Degradation of the Weld Joint:

The modified 9Cr-1Mo steel fusion weld joint due to thermal cycle produces a complex heterogeneous microstructure, consisting of base metal, deposited weld metal and the heat affected zone (HAZ) . The base metal and weld metal consist of a tempered martensite structure, with columnar grains in the weld metal. The HAZ is comprised of coarse prior-austenitic grain martensite, fine prior-austenitic grain martensite and an inter-critical structure, as one traverses from the weld fusion interface towards the unaffected base metal. This is dictated by the peak temperatures experienced by the base metal during weld thermal cycle and the phase transformation characteristics of the steel. It has been established that the localized microstructural degradation in the intercritical region of HAZ is mainly responsible for the premature creep rupture strength of Cr-Mo weld joint and can be overcome if weld residual stresses are adequately relieved by PWHT.

The lower creep rupture strength of weld joint than the base metal is due to the different types of cracking developed during creep exposure (Figure.12). Four types of cracking have been identified in Cr-Mo steel weld joint. They have been categorized as Type I, Type II, Type III and Type IV. The Type I and Type II crack originate in weld metal, propagate either through the weld metal itself (Type I) or cross over in the HAZ (Type II). The Type III cracking occurs in the coarse grain region of HAZ and can be avoided by refining the grain size. Type IV cracking nucleates and propagates in the intercritical / fine grain region of HAZ. At longer creep exposure and higher test temperature, the formation of microcracks by coalescence of nucleated cavities and propagation to the surface of the specimen produce type IV failure (figure.11).

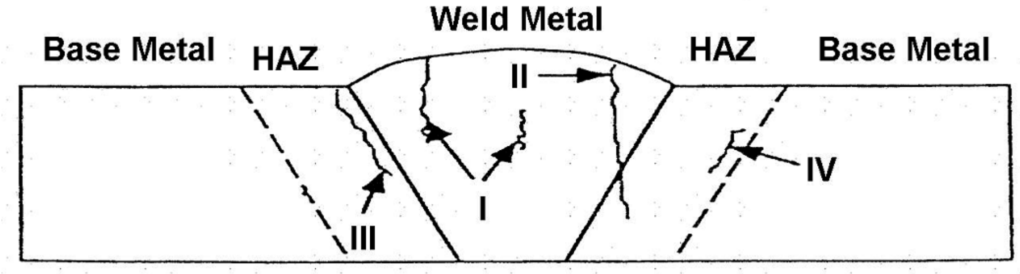
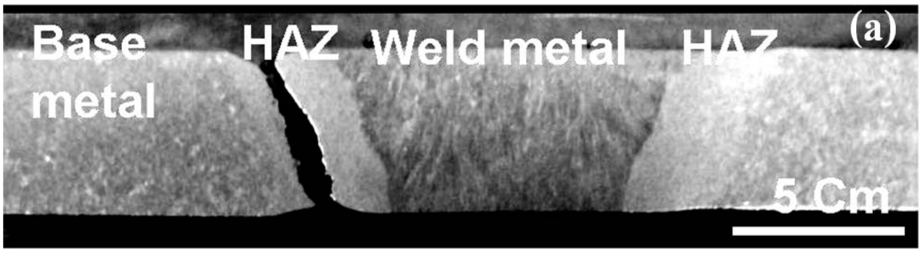


Figure.12. Locations of different types of failure in a weld geometry of the ferritic steels

The type IV cracking susceptibility, defined as the reduction in creep rupture strength of weld joint compared to its base metal, depends on the type of ferritic steel. 2.25Cr-1Mo steel is most susceptible to type IV cracking; whereas the plain 9Cr-1Mo steel is the least susceptible.



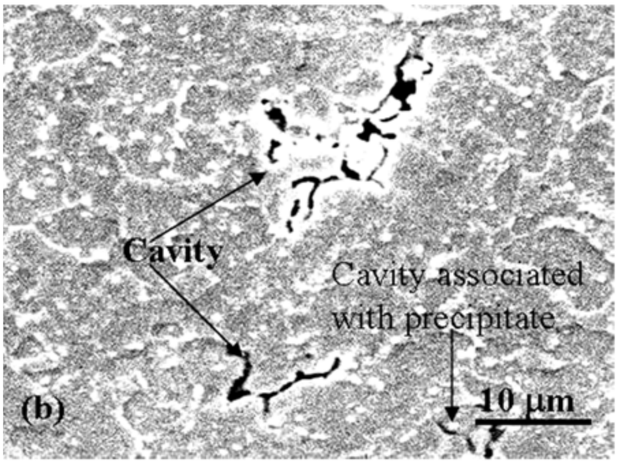


Figure.13. Type IV cracking in (a) weldment of 9Cr-1Mo steel and (b) cavities in the inter-critical region.

The relatively higher type IV cracking (Figure.13.) susceptibility of modified 9Cr-1Mo steel as compared to 9Cr-1Mo at higher test temperature is related to the precipitation of Z-phase, a complex Cr (V, Nb) N particle, in the former steel. At elevated temperatures during long term exposure, the Z-phase grows rapidly by dissolving the beneficial MX types of precipitates and accelerates the recovery in substructure with associated decrease in strength in the intercritical region of HAZ.

Although it is difficult to avoid Type IV cracking, several methods are being adopted to improve type IV cracking resistance. It is more severe in thick sections due to the imposed geometrical constraint. A design modification can be adopted to decrease the variation in tensile stresses across the welded section of the component or avoid joints in critical regions having high system stresses and relocate them in the less critical region. Strength homogeneity across the weld joint can also be improved by normalizing the component after welding. An increase in width of the HAZ can reduce the stress triaxiality such that the soft intercritical region deforms with less constraint with the consequence of reduced creep cavitation, to minimize type IV cracking tendency. The width of the HAZ can be increased both by changing preheat and heat-input during welding. Another contrasting approach to overcome type IV cracking is to avoid or minimize the width of the HAZ, to eliminate the intercritical zone. This is being attempted by employing advanced welding techniques such as laser welding. The resistance against intercritical softening can also be improved by increasing the base strength of the steel with the addition of solid solution hardening elements such as W, Re and Co and also by microalloying the steel with boron. Microalloying with boron retards the coarsening rate of $M_{23}C_6$ by replacing some of its carbon. The boron content needs to be optimized with the nitrogen content to avoid BN formation. Addition of Cu is also found beneficial. Copper is almost completely insoluble in the iron matrix and when added in small amounts, precipitates as nano-size particles to impart creep resistance. A suitable adjustment of the chemical composition of steel within the specification range also reduces the large difference in creep strength between the softened HAZ, the base metal, and the coarse grain HAZ of the joint. A weld joint of modified 9Cr-1Mo steel with low carbon, nitrogen and niobium has been reported to possess creep strength comparable to that of the base steel.

Embrittlement Issues in Materials for Clad and Wrapper Applications:

In the long term, ferritic - martensitic steels (9-12% Cr) have been identified for clad and wrapper, due to their inherent low swelling behavior. The 9Cr-1Mo steel, modified 9Cr-1Mo (Grade 91), 9Cr-2Mo and 12Cr-1MoVW (HT9) have low swelling rates even at doses upto 200dpa (HT9 shows a 1% swelling at 693K for 200dpa). However, the increase in the ductile to brittle transition temperature (DBTT) due to irradiation is a cause of serious concern for use of ferritic steels. Several methods have been attempted to address this problem, which includes modification of the steel through alloying additions, control of tramp elements by using pure raw materials and improved melting practices, and grain boundary engineering. This is an unsolved problem like Type IV cracking. However the propensity of the problem is less if the clad thickness is low, which normally is the case to ensure best heat transfer properties. For low thickness components, the triaxial stress necessary for the embrittlement does not develop, which reduces the intensity of this otherwise serious problem of embrittlement in ferritic steels.

SUMMARY:

Future trends in the global fast reactor industry are towards higher operating temperatures, higher burn-up (200 GWd/t), higher breeding rations (~1.4) and longer lifetime for reactor (60 – 100 years). These goals require several developments in materials science and technology across all components of nuclear plants, especially for fixed core component materials.

In terms of breeding ratio and sustainable growth of nuclear energy, metallic fuels are envisaged for the next generation of fast nuclear reactors in India. The fabrication, use and reprocessing of these fuels poses several challenges that are being studied currently. The fuel will have to be fabricated under remote operation in an inert atmosphere. Candidate alloying additions such as Zr to the pure metal are being considered and evaluated. Suitable corrosion resistant coatings and refractory container materials will have to be selected to minimise fuel – clad interactions. Pyrochemical reprocessing route is being developed involving molten salts at high temperatures, as opposed to the currently well-established aqueous route for oxide fuels. Metallic fuel cycle requires new waste treatment strategies to be developed.

Increase in reactor operating temperature and thermal efficiency require better coolants than the currently used liquid sodium. Cooling by gas such as He and Pb-based liquid alloys will have to be considered. This demand requires verification of compatibility of fuel and the clad material and thus affects the choice of core structural materials. Further, increased burn-up considerations at the higher operating temperatures requires novel fuel design concepts such as the annular fuel pellet. Most importantly, the current limitation on fuel burn-up, namely, void swelling of the core structural materials will have to be reduced or further delayed. Compared to currently used austenitic stainless steels, ferritic steels have a much better void swelling resistance and are capable of burn-up ~ 200 GWd/t as clad material. However their use is rendered difficult due to their poorer tensile and creep strengths at temperatures higher than ~ 873 K. Development of higher temperature tensile and creep strengths in these alloys will enable working the reactor at higher temperatures and to longer burn-ups, thus improving the economics of nuclear power production. Commercial ferritic-martensitic steels based on 9-12 % Cr compositions exhibit the highest swelling resistance. Such alloys therefore appeared ideal for fast reactor applications, but their reduced strengths above ~ 798 K has restricted their use to certain low stressed components such as sub-assembly wrappers, used to support clusters of fuel pins. To circumvent this limitation, programmes are being implemented to explore ferritic-martensitic oxide dispersion strength variants, which can possess good strength properties up to 923 K. Conventional alloy melting routes will have to be abandoned in favour of powder metallurgy techniques of ball-milling, hot isostatic pressing and hot extrusion for the synthesis of these alloys. Process optimisation for the development of 9Cr based ferritic / martensitic steels strengthened by a fine dispersion of yttria nanoparticles has been completed. The irradiation response of dispersoids and waste management aspects is being studied.

The potential candidate materials for reactors at different temperature domains, like the low, medium and high temperature domains are grouped as shown in figure. 14.

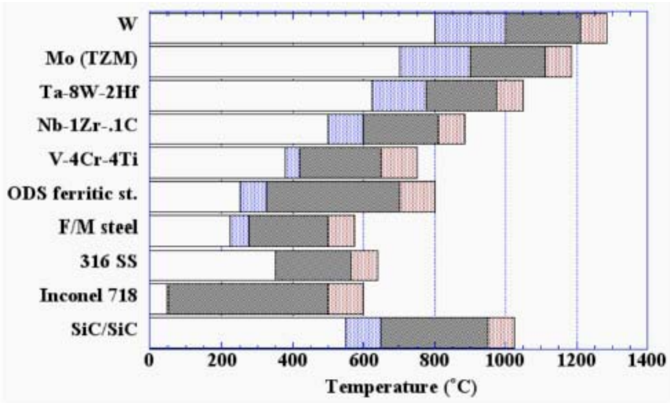


Figure.14. Estimated temperature range of candidate alloys based on mechanical properties for fission reactors, 10-50 dpa.

Safety and ease of handling spent fuel requires that the activity of the fuel assemblies on discharge from the reactor is reduced. One approach to this issue is to develop variants of the current structural materials where alloying additions that result in high activation are replaced with alternate elements to have reduced activity in the spent fuel. Solutes such as Mo and Ti are being replaced with W and Ta. The primary use envisaged for these reduced activation ferritic / martensitic steels alloys is in the fusion reactors where the radiation environment is much more severe. However, with improvements in creep rupture strength these steels can be used for future fast reactors.

Materials science, engineering and technology form an important ingredient for the safe and economic fast reactors. A number of materials and technologies that contribute to achieve the best performance using advanced materials have been highlighted in the present paper. The principles behind the design of these materials have been discussed. Materials challenges for future reactors require development of new materials through sound design principles, validation with modelling and experimental measurements, fabrication technologies and in-service inspection methods to monitor their in-reactor performance. The current trends in materials development through intense international collaborations would certainly reduce the time and cost of alloy development for future reactors.