Review article

A review of irradiation assisted stress corrosion cracking

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Abstract

The aim of this review is to assess from the available data whether irradiation in PWR primary water can adversely affect the properties of stainless steels due to irradiation assisted stress corrosion cracking (IASCC). The following aspects are examined: (i) Irradiation damage of the material. (ii) The influence of water radiolysis. Since the irradiation damage processes are similar for both PWR and BWR systems, differences observed in the intergranular cracking properties of core components of both systems must be attributable to differences in the synergistic interactions with the coolant chemistry. These aspects are analysed in detail to determine to what extent BWR experience can be used to predict IASCC in PWR core components. Several related potential failure mechanisms are also reviewed such as radiation hardening, radiation creep and helium or hydrogen embrittlement. The probable role of some or all of these failure mechanisms in core component failures observed to date, and in experiments ostensibly designed to observe IASCC, is critically examined.

1. Introduction

Irradiation assisted stress corrosion cracking (IASCC) is a term which has been used in recent years to describe intergranular cracking showing little or no ductility which can occur in heavily irradiated structural components of nuclear reactor cores. Since irradiation by high energy neutrons can affect both the material properties and the environmental chemistry and γ rays can also influence the latter, IASCC is a complex problem which is neither easy to investigate practically nor simple to understand mechanistically. Indeed in some cases, as we shall see, both in component failures and experimental investigations, it is not always certain that corrosion played a significant role while in others irradiation may only be of secondary importance in providing localized superheat to concentrate dissolved salts.

A major review of the present state of knowledge of IASCC has recently been published [1] and subsequently updated [2]. Like much of the literature cited therein, including published incidents of cracking of

stainless steel core components, the review is written largely from the perspective of designers and operators of boiling water reactors (BWRs). No attempt has yet been made, so far as is known, to review the topic with a pressurized water reactor (PWR) perspective which is the objective of this paper.

Historically, since the advent of nuclear power reactors, there have been sporadic reports of intergranular fractures in highly irradiated stainless steels (and nickel base alloys). A summary is given in Table 1 with appropriate references [1–9]. The first incidents were in early examples of stainless steel fuel cladding both for PWRs and BWRs although much less severe in the former case [3,4]. This problem was apparently improved significantly by reducing the silicon and phosphorus contents below 0.1 and 0.01% respectively and then avoided altogether by the almost universal adoption of zircaloy fuel cladding. Nevertheless, even today, irradiated stainless steel fuel cladding of advanced gas cooled reactors (AGRs) has suffered from IASCC failures following discharge to the fuel cooling ponds [1]. Potential problems with IASCC of stainless steel water

Table 1
Intergranular cracking in core components

Core component	Material	Reactor	Reference
Fuel cladding	T 304	BWR and PWR [b]	[1,3,4]
Fuel cladding	20% Cr/25% Ni/Nb	AGR [a]	[1]
Fuel element component	20% Cr/25% Ni/Nb	SGHWR (BWR)	[1]
Neutron source tubes	T 304	BWR	[1]
Control rod blades, handles + sheaths	T 304	BWR	[1,4]
Control rod cladding	T 304	PWR	[1,6–8]
Instrument dry tubes	T 304	BWR	[1]
Core spray line and sparger	T 304	BWR	[7]
Core baffle bolts	T 316	PWR	[7,9]
Absorber pins	I 600	PWR	[4]
Bolts thermal shield fuel assembly core baffle	A 286	BWR and PWR	[1,5]
Bolts shroud head fuel assembly	I 600 I 600	BWR PWR	[1] [7]
Bolts and springs core baffle fuel assembly control rod drive seal fuel assembly finger jet pump beams	IX 750	BWR and PWR	[1,4,5,7]
Control rod guide tube support pins	IX 750	PWR	[1,4,5,7]

[a] Cracking occurred in the fuel cooling pond.
[b] Attributed originally to poor water chemistry.

cooled, first wall components of nuclear fusion reactors are also now being actively investigated [10].

Examination of these cracking incidents in fuel cladding and more recently PWR control rod cladding has given rise to the proposition of a threshold fast neutron dose for the occurrence of IASCC; $\sim 5 \times 10^{20}$ n/cm^2 ($E > 1$ MeV) or ~ 1.0 displacement per atom (dpa) for BWRs and a larger dose ~ 1 to 2×10^{21} n/cm^2 ($E > 1$ MeV) for PWRs.

Consequently, it is necessary to examine the possible degradation of resistance to intergranular stress corrosion in other highly irradiated stainless steel (or nickel base alloy) core components. These may reach such dose thresholds quoted above much later than fuel or control rod cladding but nevertheless within the design life of the plant. One aim of this review is to examine the validity of these proposed neutron dose thresholds with particular emphasis on PWR components.

Two features of IASCC which set is apart from other stress corrosion cracking phenomena are the evolution of microstructure with time caused by fast neutrons and the influence of ionising radiations on the environmental chemistry. Atom displacements from their normal lattice positions in metallic materials not only give rise to progressive hardening and loss of ductility, they also lead to changes in grain boundary composition if the temperature is high enough for diffusion of point defects to take place to natural sinks such as grain boundaries. In addition neutron capture reactions yielding hydrogen and helium may contribute to embrittlement of the material, while dimensional changes due to irradiation induced creep or swelling may significantly change the applied stress. These processes are likely to be quite similar from one thermal reactor type to another and their consequences for stress corrosion susceptibility, insofar as they are known, are reviewed. The effect of radiation on environmental chemistry is also reviewed in detail and the fundamental differences between BWR and PWR coolants highlighted with particular reference to their impact on the altered microstructures of irradiated stainless steels (and nickel base alloys).

We start with a review of the environmental chem-

Table 2
Linear energy transfer and yields for reactor irradiations (12)

Radiation type	Mean LET (eV/nm)	G values; yield/100 eV						
		e^{-aq}	H^+	H_2O_2	OH	HO_2	H	H_2
β, γ	0.1	2.70	2.70	0.61	2.86	0.03	0.61	0.43
Fast neutrons	40	0.93	0.93	0.99	1.09	0.04	0.50	0.88

istry as a necessary background to interpreting the observed differences between PWRs and other types of thermal reactor.

2. Radiolysis effects

2.1. Radiolysis of water

The absorption of ionising radiations by water leads to its dissociation into several molecular, ionic and radical reaction products described by the following equation.

$$H_2O \rightarrow H_2, H_2O_2, e^-_{aq}, H, OH, H^+, HO_2.$$
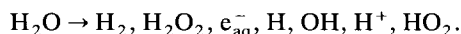
These interact in a series of known reactions, most with rather low activation energies of ≈ 3 kcal/mol, forming H_2, O_2 and H_2O_2 [11,12]. However, the overall stability of water increases with increasing temperature and yields of molecular decomposition products (H_2, O_2 and H_2O_2) are correspondingly reduced.

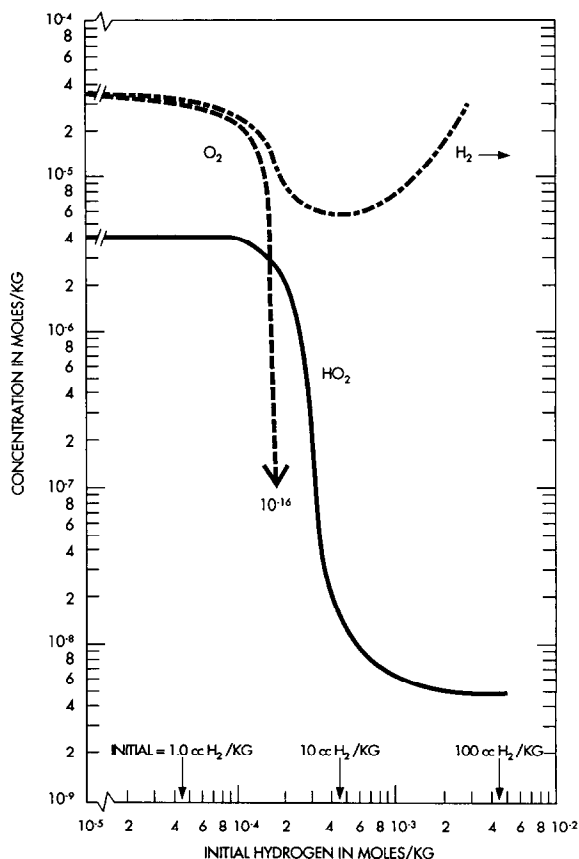The concentrations of the primary products of radi-

Fig. 1. Steady state concentrations of several radiolysis products in PWRs versus the initial hydrogen concentration [13].

olysis are controlled by the linear energy transfer rate (LET) for each radiation type and the reaction yield given by the G values; i.e. the number of molecules, ions or radicals formed for each 100 eV absorbed. G values can vary sharply with the LET so that radiation quality has a significant impact on the primary reaction product concentrations [11,12]. Typical LET and G values for γ rays and neutrons are shown in Table 2.

It can be deduced, therefore, that laboratory experiments with γ rays alone, however powerful, will not reproduce the concentrations, or perhaps more importantly, the correct ratios of primary radiolytic products occurring in power reactors where the majority of the energy absorbed by the water coolant/moderator is due to neutrons.

The influence of solutes on the yields of molecular products also varies strongly between γ and neutron radiation [11]. Solutes reacting readily with e_{aq}^- or H, reduce the yield of hydrogen whereas those reacting with OH, reduce the yield of hydrogen peroxide. This effect is observed only weakly under γ irradiation but strongly under neutron irradiation. By adding a few ml/kg of hydrogen, as in PWRs, radiolytic dissociation of water is strongly suppressed, Fig. 1 [13], whereas in BWRs without added hydrogen, a concentration of oxygen of ~ 200 ppm is observed, the precise value depending on plant design [14]. Hydrogen peroxide is only observed in BWRs if special precautions are taken before analysis to minimize its thermal decomposition as the water exits the core.

Detailed analysis of the chemical reactions of water undergoing ionising radiations in power reactors has relied mainly on complex computer based calculations using the best available data on known elemental reactions. The main check of their efficacy is comparison between predicted and measured yields of molecular decomposition products, O_2, H_2 and H_2O_2. The presence of traces of some transition metal ion impurities such as Cu^{2+} and the recently confirmed greater stability than was previously thought of H_2O_2 at high temperatures have not so far been shown to have strong effects. Despite detailed arguments concerning precise quantitative data for individual ion–molecule or radical–molecule reactions, computer codes predicting water radiolysis effects appear to do quite an effective job. This is particularly so in the context of the complexities of two phase flow in BWRs [14]. The PWR primary water situation is much simpler because boiling is prevented and water decomposition is effectively suppressed by a hydrogen overpressure [13].

2.2. Electrochemistry

In virtually all aqueous stress corrosion phenomena, the electrochemical corrosion potential is a key controlling parameter and it is important to measure it wherever possible, or at least understand the processes controlling it. Measurement of electrochemical potentials is fairly difficult in high temperature water and fraught with problems in nuclear plant, especially in the core. Nevertheless such measurements have been attempted in BWRs and with some success [15–17]. Their main objective is to establish a method of relating corrosion potential under irradiation in BWR cores to the results of calculations of water radiolysis so that corrosion potentials around the BWR water circuit may in future be calculated [17].

Compared to typical corrosion potentials on stainless steel and nickel alloy components out of core of ~ -100 to $+100$ mV (SHE), an elevation of potential by as much as 250 mV is observed in BWR cores. Similar measurements have not been attempted in PWR cores.

A key question is then: what are the reasons for the elevation of the electrochemical corrosion potential in BWRs and is a similar process possible in PWRs?

Radiation electrochemistry (usually involving only γ radiation) has been studied extensively at relatively low temperatures normally accessible in the laboratory [18]. The effects of radiation may be classified according to the location where the radiation is absorbed:

(i) in the bulk solution,
(ii) in the interfacial region between solution and electrode, and
(iii) in the electrode itself.

In initially deaerated acidic solutions, the potentials of platinum, stainless steel and nickel behave quite similarly provided there is no significant corrosion and, with the exception of platinum, are controlled completely by diffusion of electrochemically active species from the bulk solution to the electrode surface. (In the case of platinum, absorption of energy by the electrode surface itself also plays a part.) It is observed that potentials fall initially to the reversible hydrogen value despite the simultaneous radiolytic production of hydrogen peroxide. With increasing dose, potentials are observed to rise to values controlled mainly by hydrogen peroxide redox reactions because the yield (G value) of peroxide is greater than that of hydrogen.

By contrast, if a hydrogen purge is present in similar low temperature γ radiolysis experiments, an efficient radical chain decomposition of peroxide and hydroxide radicals prevents any net change in solution composition and, consequently, any significant change in corrosion or redox potentials. On platinum, however, the exchange current density for the hydrogen ion reduction reaction is increased by energy absorption by the electrode surface and the potential shifts slightly in the negative direction.

Recent experiments to measure the effect of high intensity γ radiation on the potentials of platinum and stainless steel in 288°C water have shown the same

Effect of Radiation on Corrosion Potential of 304 St. Steel & Pt in 288°C Water

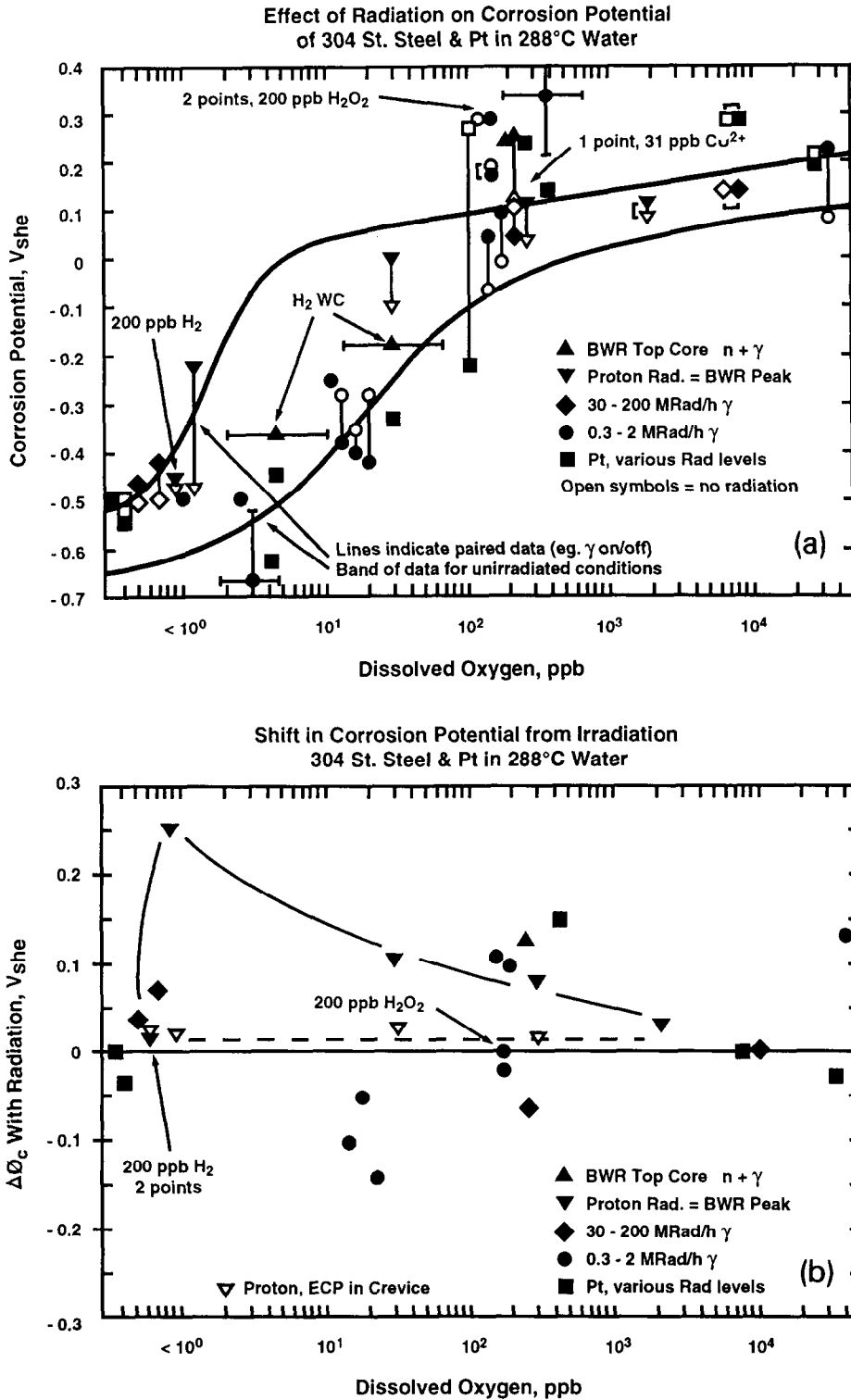## Shift in Corrosion Potential from Irradiation 304 St. Steel & Pt in 288°C Water

Fig. 2. Effect of radiation on (a) the corrosion potential of type 304 stainless steel in 288°C water (b) the shift in corrosion potential relative to unirradiated conditions [2].

general trends described above for lower temperatures [1,2], Fig. 2. However, only 150 ppb of dissolved hydrogen was sufficient to suppress any increase in potentials during γ irradiation.

Immediate extrapolation of trends observed with γ irradiation to the much higher power densities and LETs associated with in-core neutron and γ irradiation must be treated cautiously. Indeed, there is evidence in pure water and oxygenated water that proton irradiation which closely simulates the energy deposition and primary radiolytic reaction yields of BWR cores does give rise to greater positive potential shifts on stainless steel and platinum than γ irradiation alone [2]. This is corroborated by the measurements of BWR in-core potentials mentioned earlier [15–17]. Recent theoretical calculations based on a mixed potential model for electrochemical corrosion and redox potentials have reproduced these observations extremely well, Fig. 3 [19].

An underlying assumption is that the electrochemical potential is controlled by diffusion to metal surfaces of the molecular products of radiolysis, H_2, O_2 and H_2O_2. This is readily understood from an examination of the relative orders of magnitude of the rate constants of elementary ion–molecule reactions and of

typical electrochemical reactions, and also the exceedingly low steady state concentrations of ions and radicals [12,14]. These calculations also demonstrate the importance of fluid dynamics in controlling diffusion rates of electrochemically active species across the boundary layer to the metal surface.

In the presence of excess hydrogen as in PWR primary circuits, as has already been noted, the formation of oxidising species is effectively suppressed [11,13], Fig. 1. Indeed, early experiments in a power PWR into which oxygen was deliberately injected showed that the half-life of oxygen was only 12 min at a power density of 2.5 W/g [11]. It was further found that the hydrogen concentration had to be reduced well below the specified minimum (25 ml/kg) before oxygen could be detected. Therefore, there is no reason to suppose that corrosion potentials in a PWR core would be significantly different to those out-of-core and must be determined everywhere by the hydrogen ion reduction reaction, i.e. −600 to −800 mV (SHE).

Another important question concerning the effects of irradiation on electrochemical potentials is whether any unusual effects could occur in cracks or crevices.

Normally, in the absence of irradiation, the potential of stainless steels or nickel base alloys in a crevice
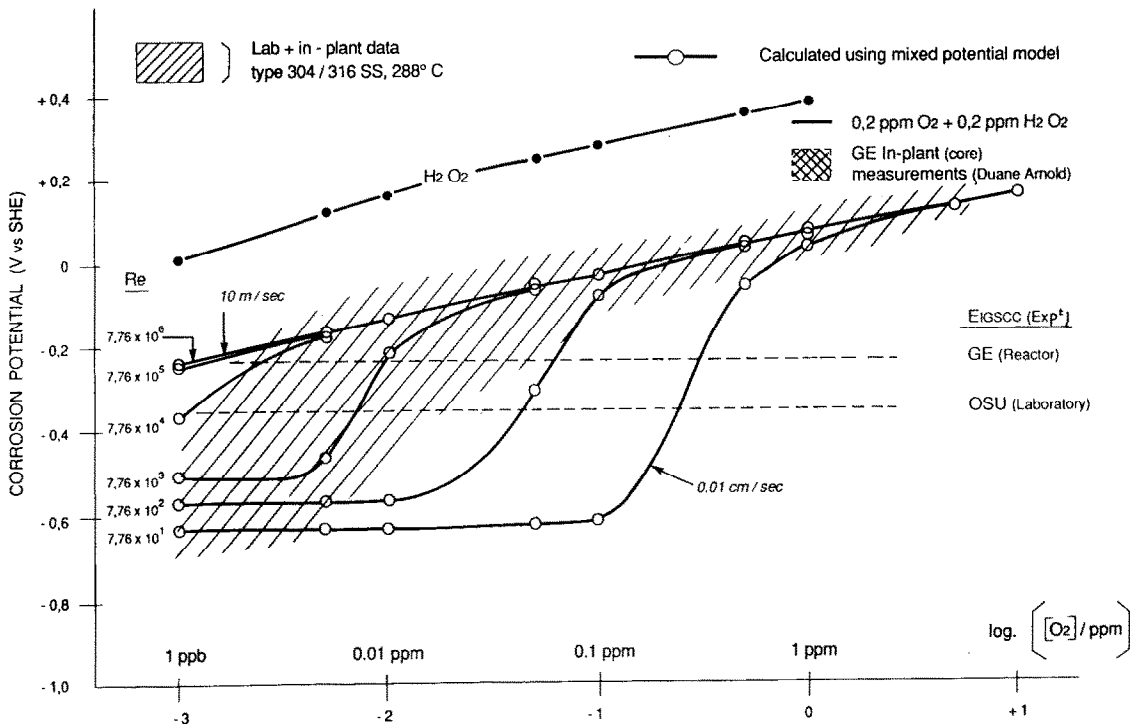

Fig. 3. Electrochemical corrosion potential versus oxygen and hydrogen peroxide concentration at 288°C [19].

is always low and close to the hydrogen redox value. If oxygenated water and a suitable anion are present at the mouth of the crevice, the crevice pH can shift strongly in the acid direction whereas in the absence of oxygen virtually no change in crevice solution chemistry occurs since there is no driving force, i.e. no potential difference between the crevice mouth and tip.

The available evidence from recent experiments using proton irradiation of a carefully selected energy from a cyclotron to simulate the LETs and G values of neutrons and γ rays in a BWR shows that the crevice or crack chemistry is not significantly changed by radiolysis; i.e. crevice potentials remain near hydrogen redox values independent of the potential outside the crevice [2]. Therefore, there appears to be little risk of any unusual crevice chemistry directly attributable to irradiation in hydrogenated PWR primary water chemistry.

It is conceivable, however, that the condition above may not be satisfied in closed crevices where local boiling might occur due to γ heating and restricted water circulation. Crevices, even closed ones, without boiling are not considered a problem, particularly where there is an initial excess of hydrogen, since there would be no net change in overall composition of the crevice solution on radiolysis. However, the chemical compounds lithium hydroxide and boric acid normally added to PWR primary water could be concentrated significantly by local boiling and lead both to a threat of crevice corrosion as well as stress corrosion cracking (e.g. caustic cracking).

2.3. Stress corrosion cracking

Experimental studies of the influence of irradiation on aqueous environmental effects on stress corrosion cracking of stainless steels (or nickel base alloys) have mainly been designed to investigate BWR conditions. However, some data have been obtained with low oxygen and/or added hydrogen which allow some judgements to be made concerning trends in PWR systems. (Stress corrosion tests on preirradiated materials and in-reactor experiments which simulate both the radiation damage to the material as well as the radiation chemistry of the environment are discussed in later sections.)

The simplest types of experiment on radiation chemistry effects have utilized relatively powerful Co^{60} γ sources [1,2,20,21], albeit at least three orders of magnitude less intense than in the core of a nuclear reactor. Slow strain rate tests have been carried out on type 304 stainless steel with prior thermal sensitization of the grain boundaries (to produce grain boundaries with chromium depletion). As deduced in the preceding sections, the electrochemical potential of stainless steel increased significantly on irradiation in oxy-genated water but decreased slightly in the hydrogen treated water. Intergranular stress corrosion cracking was enhanced in the former case but did not occur in the latter. These results show therefore that stress corrosion sensitivity of chromium depleted grain boundaries in stainless steel is controlled by the electrochemical corrosion potential established by the relevant radiation chemistry and electrochemistry.

A more complicated variant of the tests described above has been carried out recently in which crack propagation rates were measured in a precracked specimen of thermally sensitized type 304 stainless steel [2,20].

In one case [2], the irradiations were achieved using protons of a controlled high energy produced by a cyclotron, the energy being carefully chosen to simulate the radiolytic product concentrations typical of neutron and γ radiation in a BWR. The dose to the water was therefore many times that achievable from γ ray sources. Nevertheless, the results obtained on thermally sensitized stainless steels were qualitatively similar to those obtained with γ ray irradiations; i.e. a clearly defined critical cracking potential exists, above which cracking occurs. Similarly, hydrogen additions of ≈ 150 ppb typical of modified BWR water chemistry were successful in depressing the potential below the critical cracking potential for thermally sensitized type 304 stainless steel and no stress corrosion cracking was observed. In the absence of any added hydrogen, the rate of crack growth was accelerated by the higher potentials achieved with the larger radiation dose to the water compared with conventional γ ray sources. Similar observations have been made with only high intensity γ rays, although in this case a rather high threshold oxygen concentration of 500 ppb was observed [22].

The effect of sulfate impurities and γ irradiation on intergranular stress corrosion cracking in sensitized type 304 stainless steel has also been studied [22,23]. Sulfate in the absence of irradiation exacerbates cracking sensitivity and crack growth rates but with γ irradiation this bad effect seems to be suppressed. However great caution should be exercised in extrapolating this observation to reactor conditions due to the lack of comparability of radiation intensity.

An important additional point to note concerning the possible influence of the core environment on stress corrosion cracking of sensitized stainless steels is that there is a general trend for the critical cracking potential to decrease with increasing temperature [18]. It has been suggested that the temperature of in-core components may be high enough to depress the critical cracking potential for sensitized stainless steel as low as the free corrosion potential in PWRs. This is speculation, however, and no data are available to prove or disprove it.

2.4. Summary radiation chemistry

Dissolved hydrogen in PWR primary coolants is completely effective in suppressing the oxidising (and reducing) products of water radiolysis. Even the much lower concentration of hydrogen currently being evaluated in the modified BWR coolant chemistry is efficient in eliminating significant concentrations of oxygen or hydrogen peroxide and in lowering corrosion potentials below the critical value for intergranular stress corrosion cracking in thermally sensitized stainless steels.

Corrosion potentials of stainless steels and nickel base alloys exposed to strong ionising radiations in PWR primary water are deduced to be very similar to those of out-of-core components. By contrast, irradiation of water with no excess hydrogen causes the corrosion potentials of stainless steels to increase which enhances intergranular stress corrosion susceptibility of sensitized stainless steels (and by analogy nickel based alloys).

The only important effect of irradiation on crevices with restricted circulation of bulk water appears to be the possibility of concentrating salts by boiling induced by local γ heating. In PWR primary water, this could give rise to concentrated solutions of lithium hydroxide and boric acid and undesirable corrosion side-effects.

3. Radiation damage effects

Neutron irradiation of metallic materials can lead to profound changes in mechanical and metallurgical properties of potential significance to resistance to stress corrosion cracking; those of interest here are radiation hardening, radiation enhanced creep, helium and hydrogen embrittlement and radiation induced segregation.

3.1. Hardening

One consequence of intense neutron bombardment and the creation of many vacancies, interstitials and dislocation loops is a severe hardening and loss of ductility and fracture toughness of stainless steels and nickel alloys. These phenomena have been studied extensively, most commonly at the higher temperatures of interest to Fast Reactors rather than Thermal Reactors. However, it is clear that the yield stress and ultimate tensile stress of stainless steels increase significantly for fluences between 10^{21} and 10^{22} n/cm^2 ($E > 0.1$ MeV) with a concomitant drastic reduction of ductility to as low as 0.3% and only a relatively small influence of composition and microstructure on the kinetics [2]. Fracture toughness is correspondingly decreased to minimum values around 50 MPa $\sqrt{m}$ [2].

At normal strain rates, tensile fractures in heavily irradiated stainless steels are nevertheless ductile transgranular, albeit of a very characteristic appearance due to the highly localized nature of the deformation [2]. Recently, however, tensile tests on type 304 stainless steel PWR control rod cladding (described in more detail in section 4.2) have shown that the strain rate has an effect on crack morphology [6]. In fact there is an increasing tendency to substantial intergranular fracture with decreasing strain rate between 10^{-5} and 10^{-7} s^{-1}. Thus, slow deformation of heavily irradiated austenitic stainless steels can produce intergranular fracture surfaces that could easily be wrongly attributed to stress corrosion cracking.

More generally, hardening to the degree implied by residual ductility as low as 0.3% would, if achieved by cold work, normally be assiduously avoided in the interests of resistance to stress corrosion. Although hardened microstructures due to irradiation and cold work may not be strictly comparable, what little data exists for aqueous environments at ~ 300°C indicates that 10 to 50% cold worked type 304 stainless steel does not crack in hydrogenated high temperature water but is nevertheless degraded in oxygenated water [3].

Cold work coupled with crevice geometries has also been shown to enhance crack initiation in oxygenated high temperature water while 10% cold work has similarly been shown to be severely detrimental for crack propagation rates in solution annealed, type 304 stainless steel [1]. The main risk to structural integrity in PWRs may therefore occur during refueling when the pressure vessel is open to air or, in the case of fuel elements, when exposed to the fuel cooling pond environment.

3.2. Creep

As mentioned in the Introduction, irradiation enhanced creep may affect stress corrosion susceptibility via its influence on the applied stress. Loads may be relaxed under constant displacement loading or increased under non-restrained load conditions. Quantitative assessments are hindered by a dearth of data at typical water reactor operating temperatures but there seems to be no doubt that the effect is a significant one even at 288°C [2].

Another factor to consider is the sensitivity of stress corrosion in many passive metal / aqueous environment systems to the applied strain rate since it controls the rupture rate of the protective oxide film. Hence a direct effect of the irradiation creep rate on stress corrosion cracking of core structural components can be anticipated [1] with a possible synergistic interaction with any helium bubble formation from transmutation reactions.

3.3. Hydrogen and helium embrittlement

One possible hypothesis advanced to explain low ductility intergranular fractures observed in highly irradiated stainless steel core components of thermal reactors is based on embrittlement by hydrogen and/or helium, possibly enhanced by irradiation hardening and lack of ductility of the grains themselves [24]. Both gaseous embrittlers have long been considered as a potential hazard for reactor structural materials [10]. The principle sources of hydrogen to consider are the corrosion reactions and (n, p) nuclear reactions in the material and for helium (n, α) nuclear reactions.

3.3.1. Sources of hydrogen

In properly controlled water chemistry, whether of the PWR type (with hydrogen and lithium hydroxide additions) or the BWR type (pure water plus radiolytically produced hydrogen and oxygen) the corrosion rate of stainless steels will be very low, say within the band 0.1 to 1.0 mg/dm² day [11,13]. The supporting cathodic reaction is hydrogen discharge from water in totally deoxygenated PWR conditions. Even in BWR water at high temperature, the mixed corrosion potential is established with a large contribution from hydrogen evolution together with oxygen reduction [19].

Thus, a conservative estimate of the maximum corrosion hydrogen discharge rate assumes the maximum likely corrosion rate totally supported by hydrogen evolution; i.e. a corrosion current of 0.5 μA/cm² which is equivalent to about 5×10^{-8} ml H2 (STP)/cm² s. This rate of production would be enough to saturate significant thicknesses of stainless steel, 1.0 cm say, after some years although diffusion would probably be rate controlling, at least in fully austenitic steels.

Although the diffusivity and solubility of hydrogen in (unirradiated) stainless steels is well established as a function of temperature and gaseous hydrogen pressure [25], it is not so easy to estimate the equivalent hydrogen fugacity due to the corrosion reactions. Measurements of dissolved hydrogen in BWR core components have indicated values mainly between 10 and 30 wppm with a maximum of 90 wppm. There is only an apparently weak increase in concentration with neutron dose which suggests a small contribution from (n, p) reactions [26]. These results indicate an equivalent hydrogen fugacity of ≈ 10 MPa at 289°C. No similar data for stainless steels have been found for PWR conditions but a similar exercise for pressure vessel steels [27] suggests hydrogen fugacities of a similar order of magnitude. Given the similar corrosion rates of stainless steel and low alloy steel in both types of water chemistry (when properly controlled) and lack of significant galvanic differences between stainless and carbon steels in each coolant, then similar limits for equivalent hydrogen fugacity can be anticipated.

The time to reach equilibrium and the extent of hydrogen homogenization in austenitic alloys depends very much on the temperature of operation, the thickness of components and their effects on diffusion rates but is likely to take many years at temperatures around 300°C.

The period of equilibration could also conceivably be influenced by radiation damage since vacancy clusters are known to interact strongly in type 316 steels with hydrogen atoms [28]. In this study it was also noted that high energy electron predamage above 0.5 dpa produced tangled dislocations facilitating the transport of hydrogen.

Thus, overall, irradiation effects on diffusion and therefore on equilibration with the various sources of hydrogen are difficult to judge quantitatively.

3.3.2. Hydrogen embrittlement

It is well documented that the ductility and UTS of austenitic and austeno-ferritic stainless steels can be severely degraded at least at room temperature by absorbed hydrogen [29] even in the absence of irradiation damage. Unfortunately, studies of embrittlement often do not give details of hydrogen concentration measurements although more than 100 wppm could be expected in most cases. In fully austenitic stainless steels, severe degradation leading to cleavage type fracture modes has been clearly linked to the formation of α′ martensite by plastic deformation [1,29,30].

The martensitic deformation temperature (i.e. the temperature at which 50% of the sample transforms to martensite at 30% strain) can be used as a measure of susceptibility as defined by the empirical equation [31]:

$$Md(°C) = 413 - 462(C + N) - 9.2(Si) - 8.1(Mn)$$
$$- 13.7(Cr) - 9.5(Ni) - 18.5(Mo),$$

where the elemental concentrations are in wt%.

Easily transformable stainless steels such as type 304 are much more susceptible than very stable type 310 for example. Type 316 stainless steel is also relatively stable with typical Md temperatures well below 0°C. The hydrogen charging process itself may also cause the formation of ε martensite in the less stable steels such as type 304. Nitrogen strengthened steels show a much increased tendency to cleavage in the hydrogen charged condition [32].

Thermal sensitization of austenitic stainless steels has been observed, also in room temperature tests, to change the fracture mode of hydrogen charged specimens from ductile-dimple or cleavage to predominantly intergranular [29,33]. Again this can be explained in the case of easily transformable steels by the rise in Md temperature in the chromium depleted layer adjacent to the grain boundaries of thermally sensitized materials.

Even types 304L and 316L stainless steels, given a sufficiently severe sensitization, can be embrittled intergranularly by hydrogen [33].

However, the former is more sensitive than the latter, α' martensite being detected on the grain boundaries of strained sensitized type 304L but not of type 316L where ε martensite may be present. It also seems reasonable to suppose that grain boundary impurities such as phosphorus and sulphur and possibly nitrogen could also increase susceptibility to intergranular hydrogen cracking in sensitized stainless steels. As will be seen in section 3.4, chromium and molybdenum depletion together with phosphorus and sulphur enrichment are observed at the grain boundaries of heavily irradiated stainless steels.

Type 304L gas tungsten arc welds using a type 308L filler wire yielding ~ 10% δ ferrite have also been tested in a high pressure hydrogen environment [34]. These tests also showed a marked reduction in ductility and change of fracture mode, in this case the fractures initiating at the γ–δ interfaces. Extensive twinning and martensite platelet formation were observed which were believed to produce both high local stresses and high hydrogen concentrations at the γ–δ interfaces.

The influence of increasing temperature on hydrogen embrittlement of austenitic stainless steels is rather difficult to judge given the relative paucity of data compared to room temperature [30]. However, given the mechanistic explanation described earlier, hydrogen embrittlement above the Md temperature would be expected to diminish rapidly at least as far as cleavage and intergranular modes of failure are concerned. Such an amelioration of hydrogen effects with increasing temperature has been observed, even in easily transformable steels above 100°C [30]. Reductions in flow stress and ductility could nevertheless still persist at higher temperatures due to the high solubility and low diffusivity of hydrogen in austenite.

It is a mute point whether irradiation induced loss of ductility (see section 2.1) could have a synergistic effect with hydrogen and enhance ductility loss or provoke intergranular cracking in types 304 and 316 stainless steels.

As noted earlier, it is known that irradiation induced defects act as hydrogen traps [28] and at least one easily transformable steel type 301 (cold worked) has shown increased loss of ductility in 10 MPa hydrogen compared to an inert gas after irradiation to 1.5×10^{20} n/cm² ($E > 1$ MeV) (~ 0.2 dpa) [35].

3.3.3. Sources of helium

The major elements and many of the minor elemental components of stainless steel and nickel base alloys undergo (n, α) nuclear reactions leading potentially to significant concentrations of helium. A comparison between helium production rates from type 316 stainless

steel between thermal and fast reactors is shown in Fig. 4 [36]. Of particular note is the boron source which would very likely be segregated to grain boundaries and, if not specified, would probably be greater than the 0.003 wt% given in Fig. 4. Unlike hydrogen however, helium is virtually insoluble in steels and it precipitates in traps or agglomerates in bubbles. There is
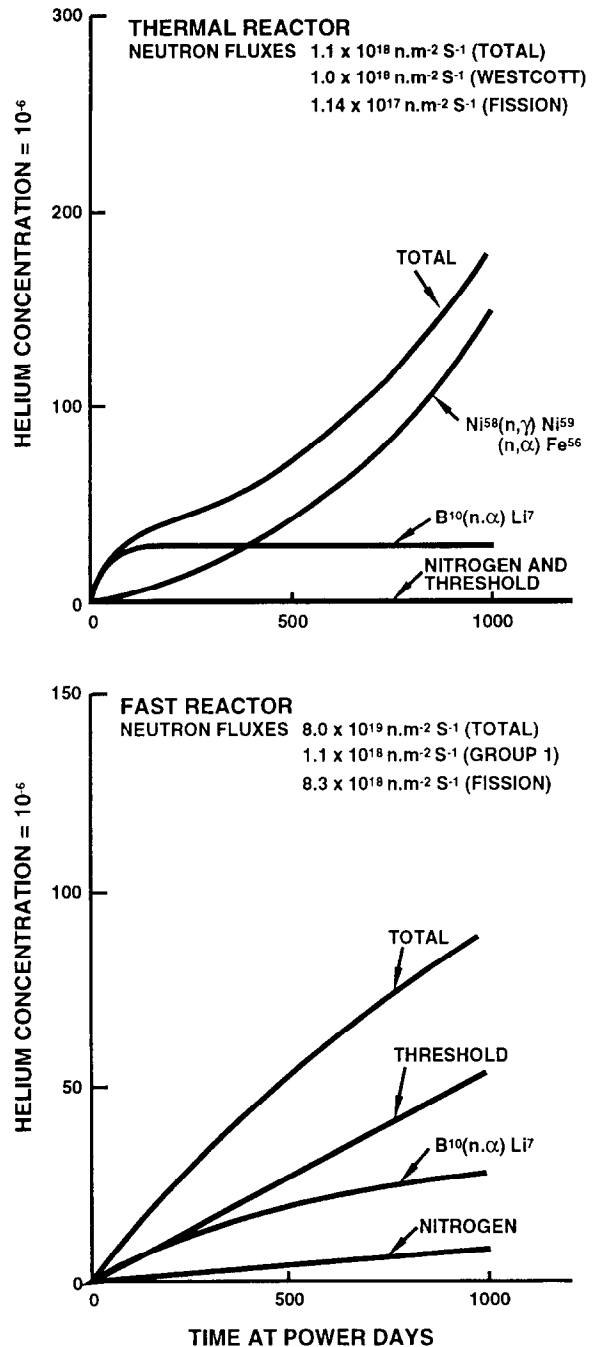

Fig. 4. Helium production in type 316 stainless steel [36].

therefore no thermodynamically defined upper limit on concentration as in the case of hydrogen and its isotopes which can diffuse relatively easily to reduce local supersaturation.

3.3.4. Helium embrittlement

Although the formation of helium bubbles both intra- and intergranularly in stainless steels is well known to cause embrittlement, loss of ductility and reduced creep strength [10], it has not hitherto generally been considered in the context of irradiation induced intergranular fracture at relatively low temperatures, e.g. ≤ 350°C.

At higher irradiation temperatures, generally above 400°C (some authorities say 500°C), some migration of helium to grain boundaries and enhanced bubble formation can be anticipated. For example, one study of two high nickel austenitic steels irradiated to 15 dpa (in EBR II) at 625°C indicated approximately a 10^3 increase in the grain boundary helium concentration compared to the average concentration of 15 appm [37]. This was sufficient to cause intergranular cracking in room temperature tensile tests in vacuum.

Similarly, in an examination of the weldability of solution annealed and 20% cold worked type 316 stainless steel with helium implanted through tritium decay, as little as 2.5 appm helium was sufficient to cause severe heat affected zone cracking [38]. In this case, the position of the crack corresponded to a maximum temperature in the heating cycle of 1150°C. By contrast, stainless steels irradiated at less than 400°C and tested at less than 400°C even with very high concentrations of helium did not show any serious losses of ductility in conventional tensile tests [39].

The lowest temperature irradiation known to give rise conclusively to helium bubble embrittlement of grain boundaries, in this case of type 304 stainless steel, was at 370°C [40].The fast neutron dose was between 1.4×10^{22} (~ 7 dpa) and 10^{23} n/cm² ($E > 0.1$ MeV) (~ 50 dpa) and the helium content 28 appm for the highest dose. The specimens were fractured in this work at 550°C in an Auger spectrometer without any reported attempt to control the strain rate. Very low ductility intergranular fractures were usually obtained, the exceptions being some examples of ductile behaviour at the lowest dose.

Reference was also made by these authors [40] to low ductility intergranular "creep-rupture" fractures observed in other work at 450, 550 and 600°C test temperatures. A volume extending about 300 nm either side of the grain boundary contributed to helium release during intergranular fracture at 550°C suggesting that only 4.5% of the boundary surfaces on average was covered with helium bubbles. Additionally, the redistribution of major and minor elements observed by Auger spectroscopy at the grain boundaries were

perfectly consistent with observations made more recently in studies directly related to the phenomenon of irradiation assisted stress corrosion cracking (see section 3.4).

In another study of the influence of irradiation temperature and tensile test temperature on the tensile properties of type 347 and 348 stainless steels, conclusive evidence of the involvement of helium embrittlement after irradiations to 4.4×10^{21} n/cm² ($E > 1$ MeV) (~ 6 dpa) was only obtained at fracture test temperatures above 500°C but less than 650°C [41]. The helium concentration measured for the highest neutron dose was 37 appm which was more than double that calculated from the fast neutron dose alone.

The decay of implanted tritium in stainless steels to helium has been used to assess the effects of helium embrittlement independent of radiation damage. Concentrations of 30 appm He^3 introduced at 200°C were found not to affect significantly the ductility of types 304L and 309S stainless steels in room temperature tensile tests at normal strain rates whereas in tests at 700°C severe intergranular embrittlement was observed [42]. Nevertheless, at low temperatures, fairly evenly distributed bubbles of helium of about 4.5 nm diameter were observed which gave rise to some increase in the measured yield strengths.

In a similar study of hydrogen isotope and helium embrittlement of types 304L, 309S, 304LW and 316L stainless steels [43], all three isotopes of hydrogen produced similar effects on mechanical behaviour at room temperature to those described in section 3.3.2. If the tritium was allowed sufficient time to decay to 30 or 50 appm He^3 followed by vacuum removal of residual tritium, ductility losses and intergranular fracture were again only observed after high temperature anneals which allowed helium bubbles to agglomerate on the grain boundaries.

Helium concentrations in excess of 200 appm have also been observed to cause ductility losses at normal strain rates in type 304L stainless steel and welds at room temperature but by enhancing microvoid coalescence and not along $\alpha'-\gamma$ or $\delta-\gamma$ boundaries as with hydrogen embrittlement. A 21Cr, 6Ni, 9Mn alloy with a similar helium content failed intergranularly at room temperature in the same study whereas the corresponding weld metal 22Cr13Ni5Mn failed by microvoid coalescence.

In summary, helium effects on the fracture of stainless steel are in general more severe than hydrogen effects at similar concentrations and particularly so if sufficient helium bubbles form on grain boundaries to provoke intergranular failure. The predicted helium production rate given in Fig. 4 could in principle be sufficient to cause problem after a few reactor cycles.

The risk would be enhanced if boron was segregated at grain boundaries or if the temperature was

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high enough, even transiently, to permit diffusion of helium to grain boundaries. The effect of operating temperature maintained below 500°C is very difficult to quantify precisely on the basis of current data, although the risk of helium agglomeration on grain boundaries seems slight at normal reactor operating temperatures.

3.4. Segregation

A detailed review of this important phenomenon for IASCC has been made by Andresen et al. [1,2] and so only the main points are reiterated here.

Fast neutron irradiation of metallic alloys causes atoms to be displaced from their normal lattice positions thus generating vacancy and interstitial point defects. Many of these recombine but at temperatures of interest to LWRs (and indeed other thermal reactors) some of these point defects migrate relatively long distances to natural sinks such as surfaces, dislocations and grain boundaries. This process leads to a redistribution of alloying elements near these sinks since different elements diffuse at different rates. Some elements such as Si, P and possibly nickel are believed to migrate mainly by interstitial mechanisms and are enriched near sinks while other solutes such as chromium, iron and molybdenum exchange more rapidly with vacancies and are consequently depleted near vacancy sinks. The competition between point defect generation during neutron irradiation and recombination gives rise to a temperature/dose rate dependence of the conditions under which segregation
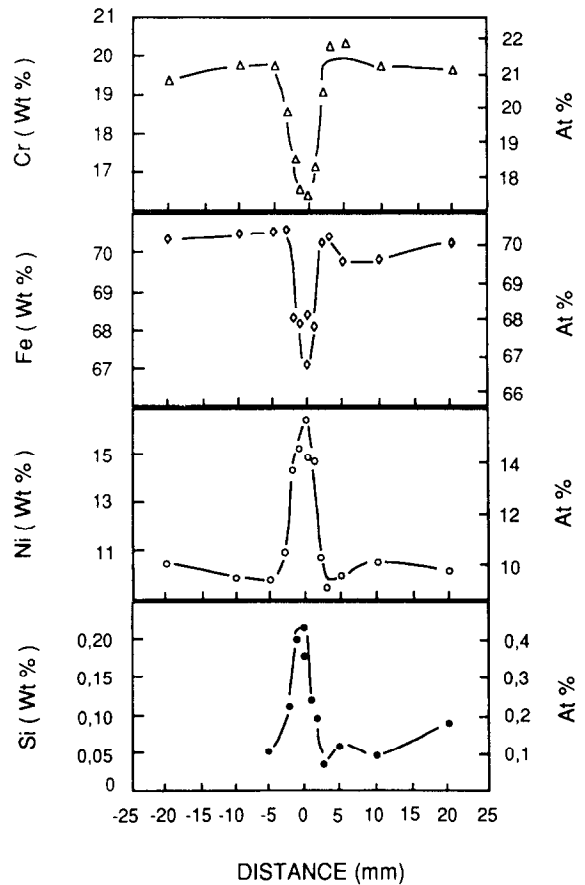

Fig. 6. Compositional profiles by dedicated STEM analysis across grain boundaries from a type HP348 stainless steel irradiated to 3.4×10^{21} n/cm^2 in a BWR [44].
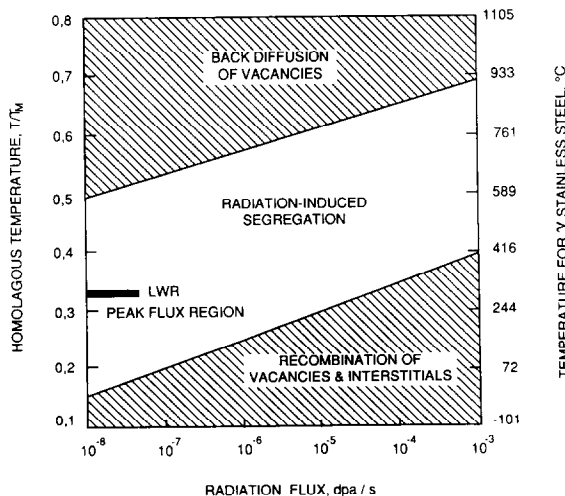

Fig. 5. Temperature/flux diagram showing the band in which radiation induced segregation is most pronounced [1,2].

is likely to occur; Fig. 5 [1,2]. Such processes are absolutely fundamental and cannot be avoided although the kinetics may be influenced by metallurgical factors.

The experimental evidence for these mechanisms of radiation induced segregation is now strongly established. The magnitude of segregation or desegregation at grain boundaries can be substantial as illustrated in Fig. 6 for a type 348 stainless steel irradiated to 1 or 2 dpa in an LWR [44]. Qualitatively, similar profiles of segregated/desegregated species have been observed in types 304, 316, 348 and 20% Cr/20% Ni/Nb stainless steel irradiated at ~ 300°C [1,2,40,44–47] and in other stainless steels and nickel alloys irradiated at higher temperatures [48,49]. Thus at 300°C, chromium and iron are typically depleted by 5 to 10 wt% from the bulk concentration in type 3xx stainless steels, even in Nb stabilized types, whereas nickel is enriched by about 5 to 10 wt% from the bulk concentration, Fig. 7 [44].
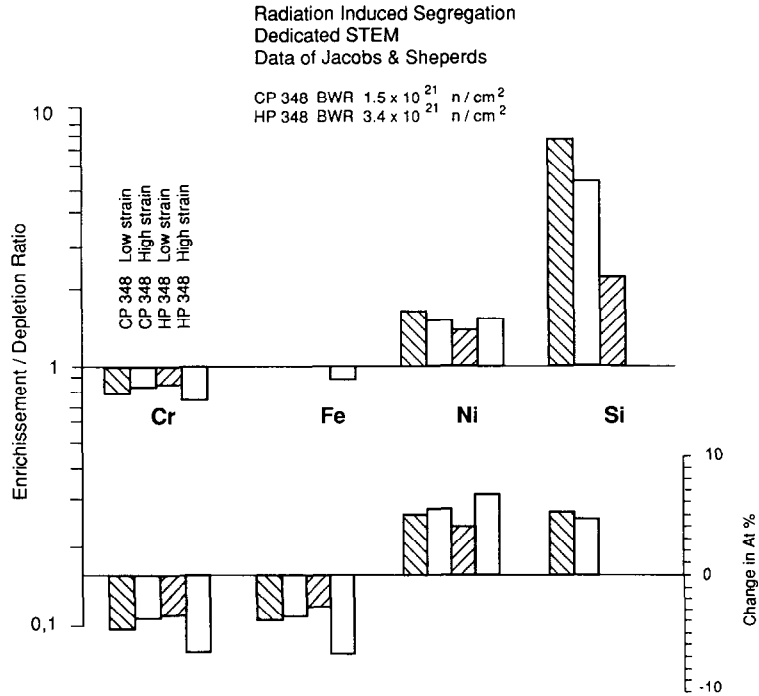
Fig. 7. Comparison of dedicated STEM analysis data from commercial purity and high purity type 348 stainless steel irradiated to various fluences in a BWR [44].
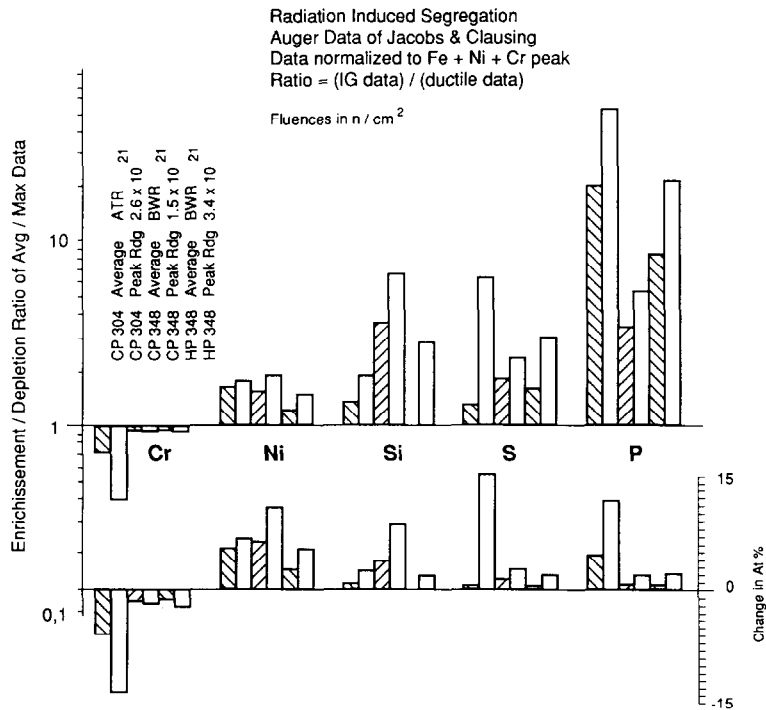

Fig. 8. Comparison of Auger spectroscopy data from commercial purity types 304 and 348 and high purity type 348 stainless steels irradiated to various fluences in an advanced test reactor or BWR [44].

Molybdenum is also depleted but to a lesser extent of $\approx 2\%$ [47]. Silicon is observed to be significantly enriched by three to five times the bulk concentration [44,45,47] even to the extent of forming Ni_3Si precipitates in stainless steels with a somewhat higher nickel content than typical of the type 3xx series [49].

The common impurity elements sulphur and phosphorus tend to be enriched at grain boundaries although the data can be rather scattered; Fig. 8 [44]. The dose dependence of segregation is illustrated in Fig. 9 [47] from which it is seen that segregation is readily detectable for doses above 10^{21} n/cm^2 ($E > 1$ MeV).

Extremely narrow segregation profiles (< 10 nm) are observed for irradiations at $\approx 300°C$ (Fig. 7). At higher temperatures, the magnitude of the segregation at grain boundaries is reduced and the widths of the zones affected are increased. Various synergistic effects between different elements are also known or suspected as having an influence on segregation. Nevertheless, good quantitative agreement has been achieved between experiment and theoretical modelling of irradiation induced segregation of certain elements, notably Fe, Ni, Cr, by the inverse Kirkendal mechanism [1,49]. At LWR temperatures, significant segregation is predicted at a dose of 0.1 dpa and saturation of the effect at about 10 dpa. Some progress is also being made in modelling phosphorus, sulphur and silicon segregation by interstitial mechanisms [1,50].

The extreme narrowness of the segregated zones at grain boundaries in stainless steels irradiated at LWR temperatures creates very great technical difficulties for quantitative characterization, to say nothing of the added complexity of working with activated alloys emitting high energy γ rays. Most success has been achieved using high resolution scanning electron microscopy with an exceedingly high brightness field emission electron gun and a beam diameter of ≈ 2 nm [44–47]. Conventional instruments with typically 10 to 20 nm diameter electron beams are unable to detect segregation on the required scale. In addition, special equipment and great care and skill are required in the preparation of the specimen foils and in the analysis of the X-ray spectra which are complicated by background γ ray emissions from the specimen. Auger spectroscopy can also be effective on the necessary geometric scale, particularly for sulphur and phosphorus, provided intergranular cracking can be provoked in the spectrometer and the γ radiation can be tolerated from the relatively large specimens usually employed [40,51]. Martensitic transformations can complicate specimen preparation for Auger or STEM studies in type 304 stainless steels, particularly high purity casts.

Hydrogen embrittlement used to encourage intergranular fracture in Auger spectrometers may also reveal the importance of different elements to those
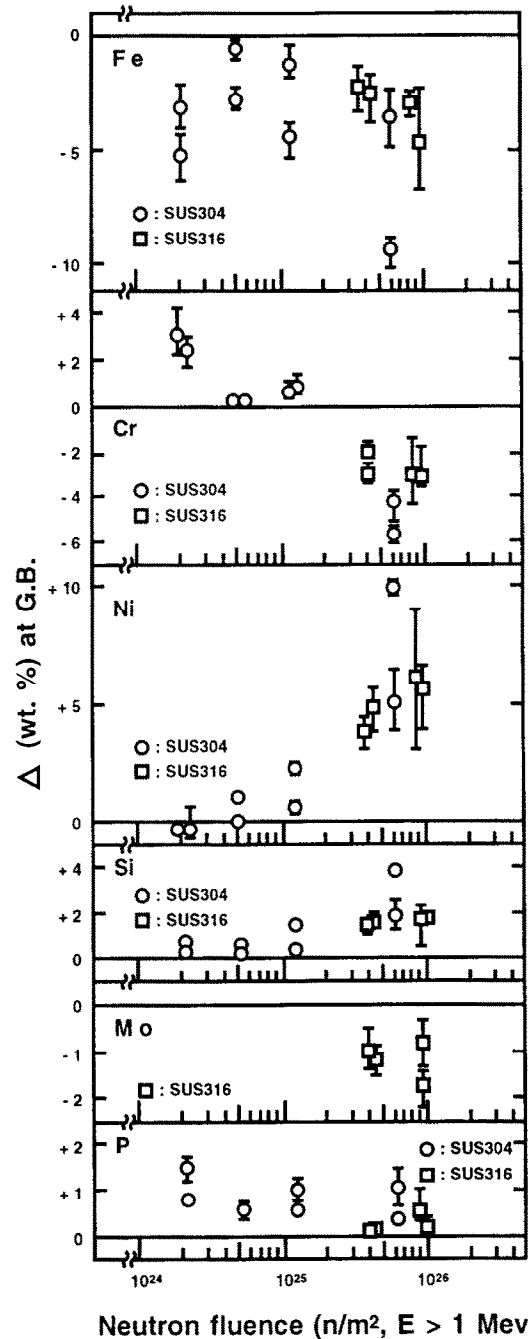

Fig. 9. Neutron fluence dependence of grain boundary segregation in types 304 and 316 stainless steel [47].

which are significant in high temperature water. Atom probe techniques can also be applicable provided again that the background radiation can be tolerated and that a grain boundary can be located sufficiently close to the tip of the probe.

3.5. Stress corrosion cracking

What then are the implications of irradiation in-
duced segregation for stress corrosion resistance in
PWR and BWR environments or indeed for standard
chemical or electrochemical tests for grain boundary
segregation? We include in this section all known data
concerning postirradiation tests. Results from experi-
ments in reactor cores are included in the next section
on in-reactor experience.

3.5.1. Grain boundary segregation tests

Of the common tests used to detect grain boundary
chromium depletion [52,53], the Strauss test has been
shown to be ineffective in stainless steels irradiated to
1 or 2 dpa which have nevertheless cracked in service
in oxygenated aqueous environments at ~ 300°C [1,49].
The width of the zone of chromium depletion of
< 13.2% appears to be a crucial parameter controlling
the efficacy of these tests.

In LWR irradiated materials this zone is less than
about 6 nm wide and is ten times narrower than typical
of thermally sensitized materials. A chromium de-
pleted width of 6 nm was found to be the minimum
width necessary for the Strauss test to respond follow-
ing irradiation over a range of higher temperatures
[49]. The EPR test would be expected to have a rather
similar response to the Strauss test and has successfully
detected chromium depletion induced by irradiation at
420°C [54]. However, there could be electrochemical
complications on specimens with high γ activities.

Boiling nitric acid tests which are also sensitive to
phosphorus and silicon segregation have also been
used to characterize irradiated stainless steels [55]. The
degree of grain boundary dissolution does appear to
vary continuously with fast neutron dose and some
correlation with PWR and BWR plant failures has
been observed [1,2,4,44,56,57].

Nevertheless, their sensitivity to phosphorus segre-
gation in particular, for which there is no satisfactory
evidence of it being important to stress corrosion in
high temperature water reactor environments and good
electrochemical arguments why it may not be impor-
tant [1], suggests again that such results could be
misleading.

An alternative deduction could be (see later) that
the failure mechanism of some in plant components,
particularly at high neutron doses > 10^{21} n/cm^2 ($E > 1$
McV) is not stress corrosion but that these nitric acid
tests reveal the microstructural changes responsible for
whatever intergranular cracking mechanism is relevant.

It is concluded that the results of all low tempera-
ture diagnostic tests for grain boundary segregation in
irradiated stainless steels (or nickel alloys) must be
treated with great caution. They can be ineffective
and/or misleading.

3.5.2. Stress corrosion cracking tests

From the analysis of component failures in BWRs
and slow strain rate tests on preirradiated type 304 and
316 stainless steels in simulated BWR water (at 288°C),
a threshold dose of 5×10^{20} n/cm^2 ($E > 1$ MeV) (~ 1
dpa) for the onset of IASCC has been deduced
[1,2,44,46,56,57,15,58,59]. This threshold has been
widely attributed to the development of chromium
depleted grain boundaries as described in section 3.4.
Moreover, typical dependence of intergranular stress
corrosion cracking of sensitized stainless steels on oxy-
gen concentration is observed. Thus, intergranular
cracking can be suppressed in deoxygenated solutions
at least for the lower neutron doses (5×10^{20} to $2 \times$
10^{21} n/cm^2 $E > 1$ MeV).

A quantitative relationship between neutron dose
above 5×10^{20} n/cm^2 ($E > 1$ MeV) (~ 1 dpa), mea-
sured grain boundary chromium depletion and IGSCC
(IASCC) susceptibility has proved elusive however [60].
Indeed, it is now clear that for type 316 steel irradiated
to a neutron dose of 9×10^{21} n/cm^2 ($E > 1$ MeV)
(~ 13 dpa), intergranular cracking cannot be com-
pletely prevented by reducing the oxygen concentration
in water at 288°C to values consistent with corrosion
potentials less than the critical cracking potential for
thermally sensitized stainless steels.

Observations that some type 304 and 316 stainless
steel PWR components exhibit a minimum fast neu-
tron dose threshold of ~ 2×10^{21} n/cm^2 ($E > 1$ MeV)
(~ 3 dpa for intergranular cracking (section 4.2) rein-
force the idea that another cracking mechanism oper-
ates in the higher dose regimes which is not related to
grain boundary chromium depletion) [1,26,8,9].

In addition, relatively recent in-reactor experiments
(section 4.1) on several different stainless steels using a
swelling capsule technique gave generally very low di-
ametral strains to failure (with the exception of one
ultra pure heat of type 348 stainless steel) whether
exposed to BWR or PWR water [61]. In fact, in both
water chemistry types the apparent threshold fast neu-
tron dose for cracking in these experiments was much
closer to that believed to be characteristic of PWRs.

We conclude therefore that irradiation induced
grain boundary depletion of chromium can explain
some observed cases of intergranular cracking particu-
larly in oxygenated BWR environments and for neu-
tron doses between about 5×10^{20} (~ 1 dpa) and $2 \times$
10^{21} n/cm^2 ($E > 1$ MeV) (~ 3 dpa). However, it does
not explain the higher dose failures and those occur-
ring in totally deoxygenated PWR environments where
corrosion potentials are well below the critical cracking
potential for sensitized stainless steels. It now seems
clear that one or more of the embrittlement mecha-
nisms discussed earlier probably play a role.

While the role played by neutron irradiation in-
duced grain boundary chromium depletion in the

IASCC of stainless steels in oxygenated water is reasonably clear, the role of other segregated/desegregated elements is much less clear. Their significance can only be assessed from some knowledge of their electrochemical characteristics and effects in other nonirradiated stress corrosion studies.

No particular significance in either BWR or PWR environments has so far been attributed to irradiation induced nickel enrichment or iron and molybdenum depletion at grain boundaries in stainless steels. However, martensitic transformations could in principle be facilitated in the grain boundary zones possibly encouraging sensitivity to hydrogen embrittlement at relatively low temperature (during plant shutdown for example). An intriguing question for PWRs is whether, after prolonged neutron irradiation, the grain boundaries could resemble those of a nickel base alloy such as alloy 600. However, the magnitudes of segregation/desegregation observed in type 3xx stainless steels, even at relatively high neutron doses, does not suggest that this is a realistic possibility.

Of the minor alloying or impurity elements, concerns have been mainly focussed on silicon, phosphorus and sulphur segregation although this often appears to be an instinctive reaction rather than derived from hard evidence other than via the doubtful means of the boiling nitric acid test [6,57]. Recent work on irradiated model alloys seems to confirm this opinion for BWR conditions [46,62].

Nevertheless, silicon and phosphorus specifications have recently been reduced significantly for LWR control rod cladding. The only known evidence for their possible significance comes from observed improvements in the resistance of stainless steel fuel cladding to intergranular cracking in the early years of LWR fuel development [1–4] and the in-reactor swelling capsules experiments [61]. From a basic electrochemical view point, it is difficult to see why phosphorus should be important in either BWR or PWR environments; it requires higher potentials as in nitric acid to dissolve. However, phosphorus could be important in other types of intergranular embrittlement.

Silicon on the other hand is highly surface active and any tendency to form silica based oxide films over grain boundaries enriched in silicon would seem to be undesirable since silica readily dissolves in high temperature water, (independent of water chemistry in the range of interest). Recent work appears to discount this possibility, however [46,62].

Sulphur segregation to grain boundaries in irradiated stainless steels is not consistently observed but is believed to act synergistically with chromium depletion in typical BWR normal water chemistry conditions [1]. Nitrogen, carbon and boron are other minor elements which could be significant for intergranular cracking susceptibility through their influence on irradiation

damage. Boron has already been discussed in the context of helium generation.

Finally, it is necessary to add a caution that general conclusions concerning grain boundary segregation in stainless steels and effects on stress corrosion susceptibility should not be assumed to apply to nickel base alloys. The relatively poor performance of alloy 600 in PWR primary water with regard to intergranular stress corrosion cracking and also with analogous higher strength alloys in the absence of irradiation suggests a different mechanism of cracking to that relevant to stainless steels. Information on irradiated nickel alloys is very sparse and it is extremely difficult to draw any conclusions or general trends from the data available for light water reactor coolants.

3.6. Summary

Radiation induced segregation or desegregation of elements at grain boundaries in neutron irradiated stainless steels or nickel base alloys is generally accepted to be an important precursor of irradiation assisted stress corrosion cracking. The process is absolutely fundamental to materials exposed to fast neutrons and becomes detectable at doses of 0.1 dpa, significant at doses of 1.0 dpa and saturates at about 10 dpa. The zones affected adjacent to grain boundaries are typically very narrow, < 10 nm wide, in materials irradiated at water reactor core temperatures, and are difficult to characterise experimentally.

Radiation hardening and radiation induced creep may also be important contributory factors to stress corrosion sensitivity.

Since radiation damage induced processes are common to irradiated components of all types of nuclear reactor, the difference between the apparent threshold neutron doses for cracking for BWRs and PWRs illustrates the importance of the synergistic interactions with the relevant environmental chemistry.

Grain boundary chromium depletion in stainless steels appears to be the main factor controlling IASCC sensitivity in BWR environments but is not important in PWR environments. Helium and hydrogen production by neutron capture reactions are also of concern because of the embrittlement they cause. There is a high probability of intergranular failure if an alloy containing intragranular helium is heated for whatever reason above ~ 450 to 500°C due to diffusion and bubble formation on grain boundaries.

4. In-reactor experience

The discussion here is divided into two parts; the first dealing with in-core reactor experiments and the

second with known component failures and their diagnosis.

4.1. Reactor experiments

Two important series of in-reactor experiments have been conducted in recent years in order to try and understand the critical parameters and to identify alloys showing better resistance to IASCC. Notably, both have been carried out in power reactors and not test reactors.

The first set of experiments has exclusively concerned BWRs [1,2]. Various self-loaded, precracked specimens of type 304 stainless steel were exposed in the high flux region of the Nine Mile Point no. 1 BWR and the crack length was monitored continuously with time. Crack growth occurred virtually immediately in the case of thermally sensitized material but a significant incubation period was noted in the case of solution annealed materials. These results were consistent with the assumption of a threshold fast neutron dose for BWRs of $\approx 5 \times 10^{20}$ n/cm^2 (≈ 1 dpa). The rates of crack growth observed were faster than those measured in the absence of irradiation. They were also consistent with the predictions of a theoretical model based on anodic dissolution of chromium depleted grain boundaries at electrochemical potentials controlled by realistically estimated core concentrations of oxygen and hydrogen peroxide. It is not obvious, however, that these remarkably successful results and model predictions are applicable to PWR water chemistry, since anodic dissolution cannot necessarily be presumed to be a relevant mechanism in the latter case.

The second set of experiments have compared both BWR and PWR systems by utilizing a capsule test method in which a mixture of alumina and boron carbide swells slowly during irradiation [61]. By using different proportions of alumina and boron carbide, the strain rate applied to the capsule wall was varied. The exterior surfaces of the capsules were exposed to the relevant reactor coolant in a fuel element position. Fig. 10 shows the results obtained in the PWR after two reactor cycles for various stainless steels and nickel alloys. In general, the results obtained in terms of diametral strain to failure were not that different from those obtained in the BWR.

Both the type 321 stainless steel and the Inconel 718 were somewhat worse in the PWR environment although the latter when correctly heat treated also did quite well. Only a high purity heat of type 348 stainless steel (S 0.007%, P 0.002%, Si 0.02% compared to S 0.009%, P 0.009% and Si 0.34% in the commercial heat) performed well in both environments. Weight loss measurements on the stainless steels in the Huey test after irradiation were also much lower in the high purity type 348 heat. This was attributed to the low alloy concentrations of Si, P and N although only the silicon content seemed markedly different from the comparable commercial heat of type 348 stainless steel. Nevertheless, subsequent experiments on different hight purity heats have failed to reproduce this favourable result [63].

In the case of the more numerous type 321 stainless steel capsules, the results were analysed in terms of the increase in diametral strain and fast neutron fluence, Fig. 11 [61]. At the lowest swelling rate, the yield strength (corrected for radiation embrittlement) was never exceeded. At higher swelling rates, it can be seen that a minimum diametral failure strain of $\sim 0.8\%$ (equivalent to $\sim 2.5\%$ elongation) was observed at a dose of $\sim 10^{21}$ n/cm^2 ($E > 1$ MeV). Comparing BWR and PWR water environments, it was observed that the latter was slightly worse.
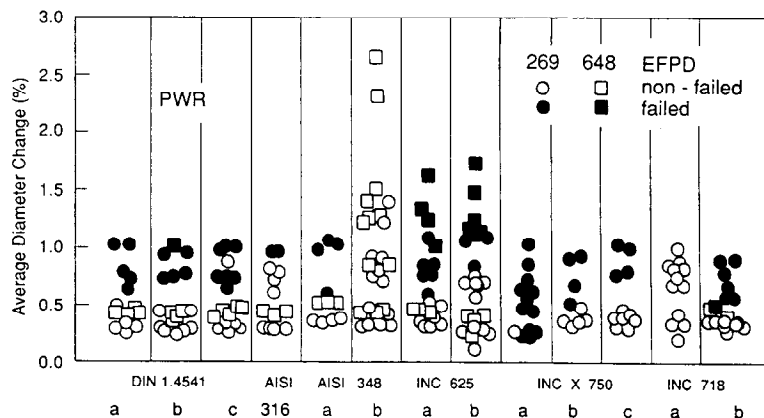

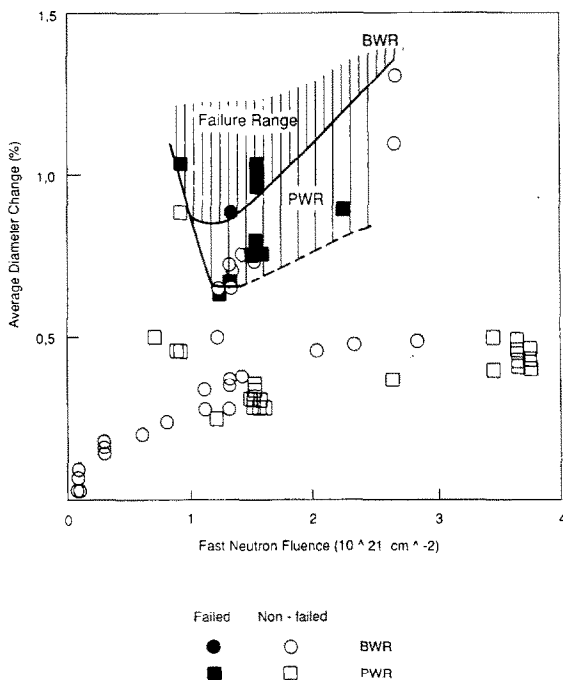Fig. 10. Strain to failure of various alloys in the core of a PWR after 1 or 2 cycles [61].

Fig. 11. Map of the range of failures of DIN 1.4541 (type 321) stainless steel samples as a function of average diameter change and fast neutron fluence [61].

This critical dose of $\sim 10^{21}$ n/cm^2 ($E > 1$ MeV) corresponds to that derived from stainless steel fuel and control rod cladding in PWRs (see later) whereas IASCC in BWRs has been associated with a lower dose threshold of 5×10^{20} n/cm^2 ($E > 1$ MeV) [1–5]. Thus the slightly worse performance indicated in the capsule tests for PWR conditions (Fig. 11) is, at first sight, at variance with practical experience. However, it is recalled that there are strong indications from postirradiation slow strain rate tests in normal BWR water chemistry and the hydrogen dosed variant for BWRs of two separate failure processes; one due to chromium depletion at doses around 5×10^{20} n/cm^2 ($E > 1$ MeV) and a second at higher doses. By implication, the second occurring at doses on the order of 2×10^{21} n/cm^2 ($E > 1$ MeV), which cannot be controlled by hydrogen additions, is also relevant to PWRs. It is suggested that this second higher dose mechanism is unrelated to localised dissolution of irradiation induced chromium depleted grain boundaries and was the cause of cracking in the swelling capsule tests. It is noteworthy that the original authors [61] concluded that radiation creep probably contributed to stress relaxation at higher doses thus leading to the ductility minimum seen in Fig. 11. In the next subsection, we shall see that intergranular cracking can be observed in heavily irradiated stainless steels when subjected to slow strain rate tests in the absence of any aqueous corrosion [6,64].

It is also recalled that cold worked (hardened) stainless steels are not apparently sensitive to intergranular cracking in hydrogenated water at 300°C [3].

It is concluded, therefore, that there is a strong possibility that the failure mechanism observed in the capsule tests on stainless steels at a high dose of $\sim 10^{21}$ n/cm^2 ($E > 1$ MeV) was mainly due to intrinsic radiation damage with a possible involvement of hydrogen/helium embrittlement.

For the capsule tests on nickel base alloys Inconel 625, X 750 and 718, no dose dependency of the failure strain was observed between 5×10^{20} and 4×10^{21} n/cm^2. The calculated diametral failure stress for Inconel X 750 was found, however, to be somewhat reduced compared to comparable data without irradiation. (In this case, the age hardened condition tested was already susceptible to intergranular stress corrosion cracking in LWR environments in the absence of irradiation).

4.2. Power reactor experience

The earliest experience of cracking in stainless steels attributed to irradiation effects occurred during the development of fuel cladding until zirconium alloys for this purpose reduced interest in stainless steels [1–4]. Such cladding failures occurred predominantly in BWRs although a few were also observed in PWR fuel elements. The cracks apparently initiated on the external surface and showed a clear dependence on neutron flux and cladding strains generated by fuel pellet swelling. Postirradiation tests, presumably at relatively high strain rates, showed only ductile rupture. At that time, the BWR incidents were associated with an apparent threshold fast neutron dose of $\approx 5 \times 10^{20}$ n/cm^2 while the PWR incidents were attributed to periods of poor water chemistry. Later, an apparent threshold of $\approx 10^{21}$ n/cm^2 was calculated [1,2,5,7]. In retrospect, the attribution to poor PWR primary water chemistry appears suspect and the threshold dose may better be associated with radiation damage mechanisms.

Intergranular cracking of other irradiated stainless steel components listed in Table 1 in BWR or other oxygenated environments have been broadly consistent with the threshold neutron doses of 5×10^{20} n/cm^2 ($E > 1$ MeV) identified above [1,2]. For stainless steel components in PWRs, the picture is more complicated. For example, failures of instrument dry tubes in PWRs have been attributed to flow induced vibration and wear.

A similar wear problem has also affected control rod cladding integrity but in this case cracking has also been observed [6,8,64]. As in the case of fuel cladding,
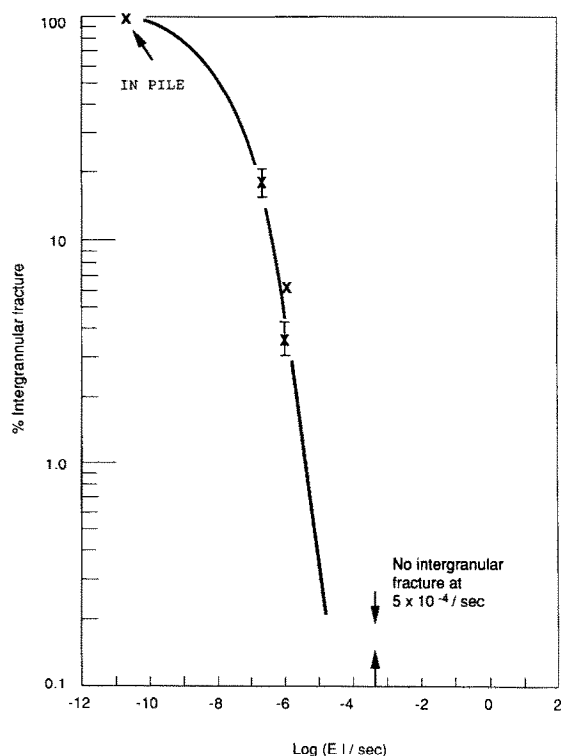
Fig. 12. Irradiated cladding tensile test results; percentage intergranular fracture versus strain rate; test temperature 600°F, argon atmosphere [64].

strains are imposed by swelling of the pin contents during neutron irradiation and consequent pellet/clad interactions. It is also not clear from evidence currently available from destructive examination whether cracks initiated from the interior or exterior of the control rod cladding.

In laboratory tensile tests in argon at 288°C however, significant intergranular cracking was observed at low strain rates of $\sim 10^{-7}$ s^{-1} but not a high strain rates of $\sim 10^{-5}$ s^{-1}, Fig. 12 [64]. The cracking initiated from the original internal surface but was attributed by the authors to a mechanical effect due to the curvature of the tensile specimen machined from the original cladding. There is also a possibility that products of neutron capture reactions with the absorber elements could influence cracking from the internal surface. The only likely one from the silver–indium–cadmium absorber would appear to be tin arising from the neutron–indium reaction. It is equally possible that the cracking is simply mechanical due to high strains applied to material with very low ductility following extensive neutron irradiation.

Recent examinations of failed type 316 stainless steel bolts in the core baffle assembly of some 900 MWe French PWRs have revealed intergranular frac-

ture surfaces [9] and IASCC has been considered as a possible cause. It is noted that the bolts which cracked were found in confined crevice zones subject to significant heating and strain cycles up to 0.5% during the heat up/cool down transient. However, if fatigue was the principal failure mechanism, then a transgranular fracture surface would be expected unless there was some serious weakening of the grain boundaries by radiation creep, hydrogen embrittlement or helium bubble formation for example. In this case, slow strain fatigue cycles could interact adversely with such intergranular damage processes (i.e. creep-fatigue) and conceivably produce an intergranular fracture surface. The imposition of a slow strain rate would in any case be expected from the earlier results on control rod cladding to increase the intergranular component of failure without the intervention necessarily of corrosion. Alternatively heating of the crevice containing the bolt could concentrate the lithium hydroxide and boric acid with potentially serious consequences for stress corrosion cracking.

Intergranular stress corrosion cracking in high strength precipitation hardened alloys such as A-286 stainless steel and Inconel X 750 has been observed frequently in the absence of irradiation. Irradiation effects are not likely to have been significant in most cases. This is particularly the case with Inconel X 750 control rod guide tube support pins where the end-of-design life fast neutron dose is anticipated to be only 5×10^{20} n/cm^2 ($E > 1$ MeV). Therefore, since failures have been observed after only a few years, it seems unlikely that radiation damage and IASCC are contributory factors. However, as heat treatments and other design improvements have now enormously improved the out-of-reactor stress corrosion resistance in PWR primary water, some care must be taken with any cases where the radiation damage may be significant over a longer period of time. In addition, any non-standard water chemistry which may be associated with closed crevices must be considered.

4.3. Summary

Stainless steel and possibly nickel alloy core component failures in BWRs are associated with a threshold neutron dose of 5×10^{20} n/cm^2 ($E > 1$ MeV) whereas a higher threshold of $\sim 2 \times 10^{21}$ n/cm^2 ($E > 1$ MeV) is typical of PWRs. In the case of BWRs, radiation induced grain boundary segregation associated with such neutron dose levels, particularly chromium depletion, and the electrochemical effects of ionising radiations on the water environment appear to explain the observed component failures. Practical solutions for BWRs are therefore directed at ameliorating these processes by hydrogen additions to the coolant as well as reducing service stresses or strains.

At the higher dose of $\sim 2 \times 10^{21}$ n/cm^2, a second mechanism of failure appears to be important which cannot be ameliorated by hydrogen additions to the environment. This mechanism may be common to both BWRs and PWRs. On present evidence, corrosion effects do not seem to be crucial and a radiation damage process may explain the observations, possibly with the involvement of hydrogen or helium embrittlement.

High strength alloys such as A 286 stainless steel and Inconel X 750 have been found to be susceptible to intergranular stress corrosion in the absence of irradiation in both BWR and PWR systems. It is difficult to determine whether any additional effect of irradiation contributed to the failures of these high strength alloys but on present evidence this seems unlikely.

5. Conclusions

Dissolved hydrogen in PWR primary water suppresses completely water radiolysis thus preventing any net change in composition and consequently any change in corrosion or redox potentials compared to those of similar materials out-of-core. By contrast, the production of oxygen and particularly metastable hydrogen peroxide in BWR cores results in anodic polarisation by up to +250 mV (SHE) compared to out-of-core components.

Fast neutron damage to stainless steels (and nickel alloys) induces significant microstructural changes including hardening, creep, helium embrittlement and grain boundary segregation/desegregation. The last of these is generally cited as the main cause of IASCC after certain neutron dose thresholds $\sim 5 \times 10^{20}$ n/cm^2 ($E > 1$ MeV) or approximately 1.0 dpa for BWRs and $\sim 2 \times 10^{21}$ ($E > 1$ MeV) or approximately 4 dpa for PWRs. However, there is presently no strong evidence for irradiation effects on cracking of nickel alloy components in PWRs which are located in relatively low irradiation dose zones.

The lower dose threshold for BWRs appears to be associated with grain boundary chromium depletion and can be ameliorated by additions of hydrogen to the coolant. It is therefore not significant for PWR primary circuit components. Other grain boundary segregants such as phosphorus and silicon enrichment could be significant for both reactor types but there is no hard evidence.

The higher dose threshold for intergranular cracking formerly associated only with PWRs also appears in the hydrogen modified BWR water chemistry. It is not obvious that corrosion plays a dominant role in this failure process. Irradiation damage could be sufficient to explain present observations possibly associated with hydrogen or helium embrittlement. The latter may be particularly important if the temperature rises, for whatever reason, above ~ 450 to $500°C$.

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