

Irradiation assisted stress corrosion cracking

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1. Introduction:

As light water reactors age and materials accumulate increasing fluence, stress corrosion cracking (SCC) is observed in more and more components. SCC normally requires the simultaneous presence of a suitable stress, a suitably hostile water chemistry, and a vulnerable material. Over the years it has been observed that as fluence accumulates, SCC is observed which could not be predicted from experiments carried out without irradiation.

In its very broadest sense, irradiation-assisted stress corrosion cracking (IASCC) can be taken to mean SCC, which is promoted by irradiation—even if the effect of irradiation is only to change the water chemistry. This definition is generally regarded as being too broad to be termed useful, and the term IASCC is normally restricted to phenomena in which the fluence leads to SCC by altering the structure of the material. The radiation which leads to IASCC can be by gamma rays, electrons, protons, or neutrons. The number of defects (generally measured as displacements per atom (dpa)) and, to some extent, their nature, depend on the type of irradiation and the energy spectrum. In LWR reactors the radiation of interest is neutrons having the appropriate energy spectrum, and all other types of radiation are of value experimentally only insofar as they can

simulate the damage caused by such neutrons.

There are two major ways in which irradiation affects the structure of LWR components. It changes the dislocation populations, leading to radiation-induced hardening and dislocation channelling (Cole et al., 1995). Irradiation also leads to changes in the local alloy chemistry, especially around the grain boundaries (Simonen and Bruemmer, 1995). Irradiation can also lead to precipitation of new phases (Garner, 1994) or destabilization of the phases present. (Yang, 1982) However, this is generally a secondary effect in LWR component failures. The cracking associated with compositional changes due to radiation-induced segregation (RIS) is generally observed at neutron fluences in the order of $5 \times 10^{20} \text{ cm}^{-2}$ (above 1 Mev) and is never observed in inert environments (Carter et al., 1995).

The irradiation-induced brittleness associated with changes in dislocation populations can be observed separately because it can lead to cracking of components at relatively low fluences and can occur in air or argon. There is no way of observing the cracking associated with RIS in the absence of the microstructural phenomena associated with dislocations. However, it is possible to distinguish failure due primarily to the dislocation-population phenomena from that associated with RIS. Dislocation channelling leads to smooth fracture surfaces, while RIS leads to typical intergranular stress corrosion cracking (Garzarolli et al., 1988; Carter et al., 1995). For practical purposes, however, most radiation-as-

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sisted fractures of reactor components are caused by a combination of the two effects.

This paper will primarily address RIS-associated cracking. The term IASCC, when used without modification, means IASCC in which grain boundary phenomena associated with RIS plays a major role. This does not imply that the cracking associated primarily with radiation hardening and dislocation channelling is unimportant. However, this paper will focus on those intergranular stress corrosion cracking problems in which RIS plays a major role.

2. General phenomenology

IASCC has been observed for many years in a variety of BWR components (Andresen et al., 1990). It was clear from the very beginning that Cr depletion near the grain boundaries was important, as well as in other cases of intergranular stress corrosion cracking in austenitic alloys. This reflects the fact that IASCC is not an entirely new phenomenon, but simply a subset of IGSCC in which RIS plays a significant role. However, it has also been clear that materials with essentially equivalent Cr concentrations and distributions can have quite different IASCC characteristics (Andresen, 1992). At one time it was conjectured that susceptibility to IASCC was due to impurities. It was thought that the utilisation of stainless steels, substantially free of nonmetallic impurities, would reduce susceptibility to IASCC, but this has since been shown not to be the case (Chung et al., 1993a).

A basic characteristic of IASCC is that it is intergranular cracking which occurs only in the presence of water and is caused by some mechanism which alters the chemistry of the grain boundaries, making them susceptible to aqueous attack. While, at least in one case, an alloy has been prepared in both IASCC-susceptible and IASCC-resistant forms (Garzarolli et al., 1995), the techniques required to produce the IASCC-resistant variety are inconsistent with forms other than sheet or tube. In general, the technical basis does not exist for predicting, for a general austenitic alloy, whether it is susceptible or not to

IASCC, or for producing a replacement for most components of material which would resist IASCC. There are several reasons for this but essentially one can not prevent IASCC in the general case because no one knows precisely what reactions to prevent other than Cr depletion. The technique for producing IASCC-resistant 346/347 cited above prevents a very large number of grain-boundary phenomena from taking place, and it appears that the critical ones are included (Hondros and Seah, 1983). This approach is not suitable for all components, or to other alloys; and it certainly is of no use to someone who has an operating reactor and wants to know how rapidly various components will degrade and what can be done about them.

3. Segregation

IASCC is influenced by the segregation (or depletion) of various components at the grain boundaries. This segregation can have several causes:

(1) Segregation during processing of the alloy (Hondros and Seah, 1983). This can be either in equilibrium (some elements tend to collect at grain boundaries for energy reasons) or in nonequilibrium (elements may be enriched or depleted at grain boundaries by phase transformation, diffusion-induced grain boundary motion etc.)

(2) Segregation effects due to radiation damage (Marwick et al., 1979; Wiedersich et al., 1979). Neutrons (or other massive particles) produce Frenkel pairs in metals. Most interstitials annihilate quickly with the vacancies migrating to grain boundaries. One consequence is that slow-diffusing substitutional species (such as Ni in stainless steels) are enriched at the grain boundaries and fast-diffusing substitutional species (such as Cr) are depleted. This is the inverse Kirkendall effect. Another important effect arises from the fact that some interstitial impurities bind to defects, and thus vacancy fluxes cause interstitial-impurity fluxes by a process called vacancy drag.

(3) Many nonmetallic impurities in steels are bound in inclusions. If radiation decomposes inclusions (e.g. by transmutation), the liberated atoms may segregate to grain boundaries either for straightforward chemical reasons or due to RIS.

Segregation during processing, especially equilibrium segregation, has been studied for more than a century and there is an extensive metallurgical literature on the subject (Hondros and Seah, 1983). RIS, however, has not been extensively studied. Good models and good data exist for Cr and Ni motion in austenitic alloys (Marwick et al., 1979; Wiedersich et al., 1979), but there are no models which will permit even semiquantitative prediction of the RIS of semimetals and interstitial elements. One part of the problem is that the inverse Kirkendall effect is partly balanced by other effects. It also seems that the motion of nonmetal atoms is strongly affected by bonding effects, which are much more difficult to model than the simple diffusion phenomena which control Cr and Ni segregation.

4. The experimental data base

There are several sources of IASCC data. The obvious source is specimens of components from operating reactors. These specimens have seen the actual environments in reactors and in that sense are typical of the materials which are actually failing. On the other hand, investigators have no way of specifying the chemistry and microstructure; if one wants to examine, e.g. a high-S, low-Si specimen, one is wholly dependent on finding a component which has the desired chemistry and is in a reactor whose operator is prepared to provide the laboratory with a specimen. Also, some specimens are from gas-cooled or breeder reactors, and one question must be addressed— whether the differences in neutron energy spectrum lead to significant differences in IASCC behavior?

Another source is specimens of known alloy chemistry and thermomechanical history which are irradiated in material test reactors (Chung et al., 1993a,b; Garzarolli et al., 1995; Chung and Karlsen, 1996). The data from these are in some

ways the most useful when trying to determine what factors control IASCC and thus determine residual life, necessary inspection intervals, and other important characteristics of aging reactors. However, this is a fairly small data set due to the low availability of experimental reactors and the cost involved in the production of such specimens.

A third source is proton-irradiated material (Was and Allen, 1993; Carter et al., 1993, 1994). The use of protons instead of neutrons for irradiation makes possible the rapid, inexpensive production of large numbers of specimens with significant fluence. Protons produce far fewer activation products than neutrons, so the resulting specimens are much easier to characterize, test and dispose of. There are two disadvantages. Firstly, protons can only produce significant damage quite near to the surface. It is impractical to produce significant, reasonably homogeneous damage deeper than approximately 50 microns. Secondly, it has not been established whether the RIS effects of protons and neutrons are the same or not. It seems plausible that specimens with equal damage as measured by dpa should have similar RIS characteristics but this is not certain. Protons not only react differently with atoms than do neutrons, but proton damage is collected in a much shorter period and this certainly has some effect as back-diffusion tends to counter the inverse Kirkendall effect.

Specimens are also available which have been electron-bombarded (Kato et al., 1992) or ion-bombarded (Bruemmer, 1991). In these cases, there is less confidence that the damage is similar to that sustained in reactors as different types of radiation produce quite different levels of Cr depletion in grain boundaries (Was and Allen, 1993). Furthermore, since these experiments are more relevant to fusion reactor materials problems, the alloys studied are frequently not typical of those found in LWRs.

5. Test data

Specimens are tested to obtain some measure of their vulnerability to IASCC and to measure various microscopic characteristics which may corre-

late with IASCC. Eventually, it is hoped that it will be possible to crosswalk the data and establish unequivocally what microscopic characteristics correlate with IASCC resistance.

The most generally accepted mechanical test is to fracture a specimen and observe the fraction of fracture surface which shows the basic characteristics of IASCC (Chung et al., 1993a). Crack-growth measurements (Chung and Karlsen, 1996) are also carried out but are more difficult. Other mechanical tests are occasionally employed, especially on proton-irradiated specimens. Shear ductility characteristics measured by shear-punch tests can be used to estimate tensile stress-to-failure values but the development of the correlation requires a significant body of shear-punch and tensile-test data on similar alloys at the same temperature, thus shear-punch testing is a technique for expanding an existing tensile-testing data base rather than developing independent data.

Data on grain boundary chemistry is generally collected in one of two ways. Fracture surfaces can be studied by scanning Auger spectroscopy (Bruemmer, 1991; Chung et al., 1993a,b; Bruemmer et al., 1995). Scanning Auger is useful in detecting very small amounts of material on grain boundaries, and can be combined with sputtering techniques to obtain depth-profile information. Unfortunately, it is not very precise, presenting particular problems when peaks lie close together. The other commonly used technique is energy-dispersive X-ray spectrometry (EDS) which is carried out with a scanning transmission electron microscope and a field-emission gun (FEG-STEM) (Chung et al., 1993a,b; Walmsley et al., 1995). This technique measures profiles of selected elements across a grain boundary.

6. Observations

IASCC is not a problem in the absence of water; IASCC is not a problem during experimentally accessible time frames if the electrochemical potential of the water is always below approximately -140 mV SHE (Indig et al., 1992). IASCC is almost always associated with Cr deple-

tion in the grain boundaries. Enrichment of Ni in grain boundaries tends to suppress IASCC (Chung et al., 1996a).

Beyond these points almost all conclusions about the effects of various impurities are debatable. The following views seem to be consistent with most of the available data (Chung et al., 1993a; Garzarolli et al., 1995; Chung and Karlsen, 1996).

The effect of P in the grain boundaries is small and cannot be accurately estimated due to the experimental noise. However, there is evidence, that under certain circumstances, it can reduce susceptibility to IASCC.

Li, Si, C and B appear to reduce susceptibility to IASCC in the grain boundaries.

O, N and V appear to increase susceptibility, particularly S.

There is a body of experimental data which correlate susceptibility to IASCC with F concentration in the grain boundaries. The mechanical testing data are not disputed but the detection of F in the grain boundaries at the levels in question is difficult and controversial and resolution of the issues related to interpretation of the grain boundary composition measurements has not been achieved.

The solubility of F in austenitic alloys is extremely low. Secondary-ion mass spectrometric (SIMS) measurements indicate that in some parts of reactor internals (especially core shroud welds), F contents can be in the order of 100 times the best estimates of solid solubility. It is not known exactly how F is distributed but it appears that there is some F in inclusions, especially MnS-type (Chung et al., 1993a). Decomposition of these inclusions by transmutation can lead to the release of significant F in a material in which the equilibrium solubility is extremely low, and where it is reasonable to expect that this will lead to F accumulation at the grain boundaries, with the transport probably occurring by vacancy-drag mechanisms. Unfortunately the Auger F peak is very close to a major Fe peak, and so the Auger grain-boundary chemistry data cannot be interpreted unambiguously (Chung et al., 1996b). Further research using SIMS, which does not have this disadvantage, may clarify this issue.

Chung et al. (1993a,b, 1996a) describe both evidence that F contributes to SCC in austenitic materials, and plausible mechanisms for this interaction. There are also parallels with the role of Cl in grain boundaries in Fe (Buchwald and Clarke, 1989) and Cu (McNeil and Mohr, 1992). What is lacking at present, unfortunately, are unambiguous parallel test data for identical alloys with and without F in the grain boundaries, coupled with unambiguous measurements of the grain boundary F concentrations. It would also be helpful to have a clearer understanding of how F can get into the inclusions. The inclusions precipitate from a melt in which the equilibrium solubility of F, while not precisely measured, is generally accepted to be very small, and where CaF_2 inclusions are extremely rare. It may be that the electrochemical nature of the electroslag remelting process plays a role in this. It would be helpful to have measurements on parallel samples prepared by ESR with and without fluoride additions to the slag.

7. Conclusions

Irradiation assisted stress corrosion cracking, like primary water stress corrosion cracking, is a special case of intergranular stress corrosion cracking. Some of the factors involved are not important and some of the phenomenology is not observed in other types of IGSCC but it is all one basic phenomenon and entirely separate models are not required.

No one, as yet, has a sufficient understanding of IASCC to predict the effects of thermomechanical history and the amounts and distribution of various impurities on the nucleation of IASCC cracking, or the growth rates of IASCC cracks. This implies that, as yet, *ab initio* calculations cannot be used to provide detailed guidance either for inspection intervals or for the evaluation of overall structural integrity, which in turn implies that IASCC research is not as effective for reducing conservatism in various regulatory decisions as it will be when there is a clearer understanding of some of the mechanistic effects.

IASCC has primarily been a BWR problem

because of the water chemistry in BWRs (and particularly the water chemistry used previously in BWRs). This means that IASCC occurs at much lower fluences. However, as PWRs approach the end of life, there will be more problems in these reactors as well. Research on IASCC in PWR applications is being expanded to address this.

There are no clear answers to such questions as to how one should maximise the resistance of an alloy to IASCC and how long a component—especially a damaged component—will last in service but there is reason to believe that such answers may begin to emerge in the relatively near future.

It will be necessary for engineers involved in the operation of power plants (and those involved directly in regulation) to decide how such answers can be used. Some components are replaceable, and in the case of such components, advances in the understanding of IASCC will make it possible to choose materials and fabrication processes which lead to greater resistance. However, many components are very difficult to replace, e.g. core shrouds and their support structures. In these cases, the new scientific knowledge can be applied to estimate residual life and the consequences of repairs or other mitigative measures, and to permit better estimates of required inspection intervals.

It is worth considering what conjectures appear to be supported by the data available at present. The following conjectures seem reasonable: (i) 304 NG is more resistant than 304; (ii) 316 is more resistant than 304; (iii) anything which promotes depletion of Cr in grain boundaries aggravates IASCC; (iv) anything which enriches the grain boundaries in Ni has at least a mildly mitigative effect on IASCC; (v) while the role of F is not understood, avoiding welding fluxes which contain F and using alloys made by processes which involve relatively little CaF_2 appear to be reasonable precautions; (vi) components which have not been exposed to relatively high levels of dissolved O_2 are less susceptible to IASCC than those which have, even if the exposures were relatively brief.

For a more complete and technically detailed exposition of this material, the reader is referred to a forthcoming paper by Dr Chung Hee et al. in *The Journal of Nuclear Materials*, 1997.

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