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Mechanisms of radiation-induced degradation of reactor vessel materials [1]

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Abstract

Fast neutrons are usually considered the source of various radiation effects caused by atom displacements, such as embrittlement, swelling, and creep. However, other reactions may contribute to atom displacements under certain conditions. These additional sources of displacements include those caused by thermal neutron capture recoils, γ-induced energetic electrons, and energetic particles emerging from transmutation reactions. In reactor vessels, for example, special circumstances may be encountered where these reactions become significant or even dominant with respect to fast-neutron-induced displacements. Key considerations describing these relative contributions are described. Inequalities are derived giving requirements among materials parameters and irradiation conditions to make each process significant with respect to fast neutrons. An example of the application of these conditions is given, covering the explanation of 'early' embrittlement in the HFIR reactor vessel.

1. Introduction

Radiation effects in nuclear reactor pressure vessels have been subject to continuing extensive scientific studies and engineering evaluations for more than four decades. Reactor vessels are constructed predominately of ferritic steels. These steels, in the aggregate, constitute by far the most massive neutron irradiated structural material. Although the doses accumulated are generally low, $\ll 1$ dpa, the corresponding changes in mechanical properties can be large. Hardening and embrittlement are the primary causes for concern. The embrittlement is manifest in potentially large increases in the ductile-to-brittle transition temperature compared to unirradiated values.

The microscopic causes of embrittlement lie in obstacles to dislocation motion, or hardening centers, as well as changes in the composition and structure in interfacial regions. Hardening centers can include point defect clusters, impurity-defect complexes, copper-rich precipitates and other precipitates, for example [1,2].

In spite of the fact that this collection of features can be diverse and complex, their formation depends upon a common basis — the production of vacancies and self-interstitials by irradiating particles. Hardening centers, essentially any imperfections in the crystal lattice, can be generated directly in cascades in the form of dislocation loops or three-dimensional nanoclusters, for example. They can also be created by gradual aggregation caused by long range diffusion of defects.

In turn, this essential point defect generation can be caused by a number of distinct mechanisms. These include energetic displacement by fast neutrons in elastic or nonelastic reactions; (n, γ) reactions leading to nuclear recoils; charged-particle-emitting reactions such as (n, α)

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or (n, p), where both the emitted particles and the recoiling nucleus may cause displacements; and interactions initiated by high energy γ-rays released in fission reactions or in (n, γ) reactions, for example.

The purpose of this paper is to assess the relative importance of several displacement mechanisms under various irradiation conditions in contributing to embrittlement.

2. Mechanisms

In reactor components, fast neutrons are typically considered the main source of radiation effects. However, in principle and in practice, other reactions can contribute to atom displacements. Special circumstances may be encountered where these alternative mechanisms may become significant with respect to fast neutrons. Several reactions are considered below. These results will each be compared to those for fast neutron displacements.

2.1. Recoils from (n, γ) reactions

Thermal neutron reactions in which a γ-ray is emitted can cause displacements by the recoil of the nucleus. This type of reaction can be important in highly thermalized neutron spectra. Fig. 1 shows the displacement cross-section of bcc iron as a function of neutron energy [3], i.e., that quantity which, when multiplied by neutron fluence, gives directly the displacement dose in dpa. For energies near 1 MeV, the displacement cross-section is about 10^3 b. This is the applicable value for fast reactors or for the fast portion of the spectrum in mixed-spectrum reactors.

After going through a minimum of about 0.1 b near 1 keV, however, the displacement cross section increases with decreasing neutron energy. In the range of 0.01 to 0.1 eV, i.e., thermal neutron energies, it reaches about 10 b.

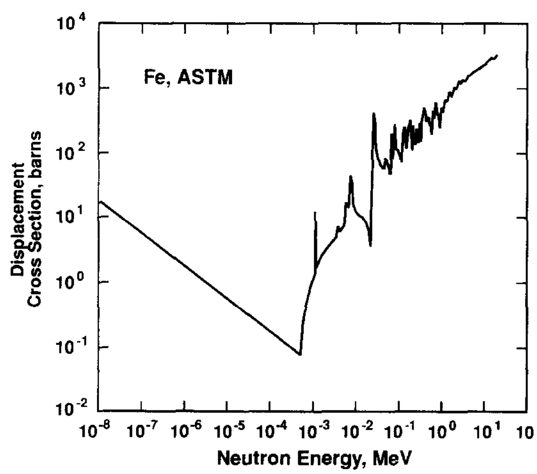

Fig. 1. Displacement cross-section as a function of energy, after Ref. [3].

2.2. Reaction products from (n, α) reactions

A charged particle reaction that is of potential importance in pressure vessel steels is the $^{10}B(n, \alpha)^7Li$ reaction. Boron occurs as an impurity in steels and has also been included deliberately in various types of structural materials in order to study the effects of the introduced helium on microstructure and properties [4–9]. The contribution to displacement damage by the ^{10}B reaction was evaluated quantitatively in Ref. [6]. Using the nomenclature of Ref. [8], we can write the damage in displacements per atom, dpa, created in the material by this reaction as

$$d_B = p_B q_B r_B g. \tag{1}$$

Here p_B is the fraction of He produced per initial ^{10}B as a function of time,

$$p_B = 1 - \exp(-\sigma_\alpha \phi_t t), \tag{2}$$

where σ_α is the thermal neutron helium production cross-section, and q_B is the fraction of ^{10}B to total B initially in the alloy — for natural boron, q_B is about 0.2. The quantity r_B is the fraction of B to all atoms in the alloy, and g denotes the number of displacements generated per helium atom produced.

The reaction can be written as

$$n + {}^{10}B \to {}^4He(1.775\ MeV) + {}^7Li(1.015\ MeV). \tag{3}$$

Relationship (3) leads to the damage energy $T_d = 20.2$ keV, of which 28% is contributed by the ^{4}He and 72% by the ^{7}Li [10]. Using the standard NRT form [11] to obtain displacements,

$$N_d = \frac{0.8 T_d}{2 E_d}, \tag{4}$$

where N_d is the number of displaced atoms and E_d is the (effective) displacement threshold energy. For $E_d = 40$ eV, we obtain $g = 202$ dpa/apa He, or, equivalently 1 dpa for each 4,950 appm He produced.

2.3. Photoelectron and photonuclear reactions

Irradiation by γ-rays can cause displacement damage in reactor vessels. There can be several origins of these γ-rays. For example, a strong source can be the fissioning fuel in the reactor core. Another source can be core and peripheral structural materials that interact with thermal and fast neutrons and undergo reactions in which γ-rays are emitted. These then may cause displacements when the γ energy is transferred to electrons, or when atomic nuclei interact with the γ-rays.

The γ-ray/electron reactions of interest are Compton scattering, pair production and photoelectric effect. The Compton effect can be described as an elastic collision of the photon with an atomic electron, where an energetic electron emerges, together with a scattered photon of degraded energy relative to the incident photon. In pair

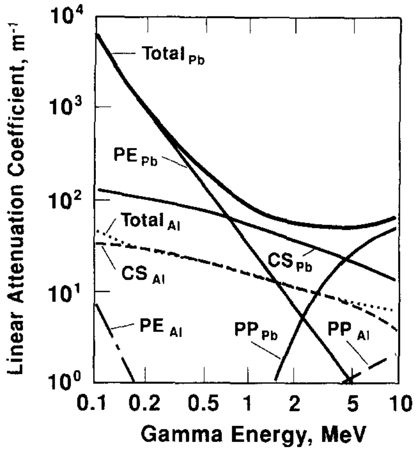

Fig. 2. Linear attenuation coefficient as a function of γ-ray energy for Al ($Z = 13$) and Pb ($Z = 82$), after Ref. [12]. Totals are shown as well as the components contributing; photoelectric effect (PE), Compton scattering (CS), pair production (PP).

production, a photon of energy E_γ greater than 1.02 MeV is annihilated. An electron–positron pair is created, each particle with kinetic energy $(E_\gamma - 1.02)/2$ MeV. In the photoelectric effect the γ-ray is absorbed by an atom and an energetic electron is emitted.

Fig. 2 shows these contributions to γ-ray attenuation as a function of energy in the relatively light and heavy metals Al and Pb [12]. The result is expressed in terms of linear attenuation coefficient or macroscopic cross-section. This is the reaction cross-section of an atom for the particular process, taken in a product with the atom density. The photoelectric effect is important at low energies and pair production is important at high energies. In the intermediate energy range of most interest for fission reactor applications, Compton scattering dominates γ-ray attenuation.

Photonuclear reactions that potentially can produce displacement damage are, for example, (γ, n) reactions giving rise to energetic neutrons and nuclear recoils. In fissionable materials, photofission reactions releasing large amounts of energy available for displacements may be induced by γ-rays. In general, however, photonuclear reactions are not as universal as the photoelectron reactions, and tend to occur only in special nuclei that are very light or very heavy. Fig. 3 shows the (γ, n) reaction with ^{9}Be, which has a threshold below 2 MeV.

3. Comparisons

It is convenient to take fast neutron displacement reactions as a standard for comparison, in order to evaluate the relative importance of the mechanisms described above. For the sake of definiteness, we consider other displacement mechanisms significant with respect to fast neutron displacements when their relative magnitude reaches 10%.

From Fig. 1 and the discussion above, we can then immediately write the inequality below as the condition for which thermal neutron induced displacements become significant (≥ 10%) with respect to those from fast neutrons.

$$\phi_t/\phi_f \gtrsim 10. \tag{5}$$

Here ϕ_t and ϕ_f denote the thermal and fast neutron fluxes, respectively.

Turning now to the ^{10}B reaction, we make a similar comparison from the discussion surrounding Eqs. (1)–(4). Taking the ratio of displacements per atom, d_B, from the boron (n, α) reaction to that from fast reactions, d_f, gives

$$\frac{d_B}{d_f} = \frac{q_B p_B r_B g_B}{\sigma_d^f \phi_f t}. \tag{6}$$

For $\sigma_\alpha \phi_t t \ll 1$, Eq. (2) may be written as $\sigma_\alpha \phi_t t$ and we may write the inequality

$$\frac{d_B}{d_f} \approx q_B r_B g_B \frac{\sigma_\alpha}{\sigma_d^f} \frac{\phi_t}{\phi_f} \gtrsim 0.1, \tag{7}$$

as the condition for which the boron-induced displacements become significant with respect to fast displacements. As a condition on the fraction of boron contained in the alloy, r_B, this becomes for natural boron ($q_B \sim 0.2$),

$$r_B \gtrsim 6 \times 10^{-4} \frac{\phi_f}{\phi_t}. \tag{8}$$

For example, from the inequality (8) for a thermalized spectrum where $\phi_t \sim 10\phi_f$, boron will contribute more than 10% of the displacements relative to fast neutrons if the boron content in the alloy is $\gtrsim 60$ appm (under the condition that the thermal fluence is low enough so that $\sigma_\alpha \phi_t t \ll 1$).

The relative importance of displacements from γ-rays can be compared in a similar way. Fig. 4 shows the γ displacement cross-section for iron, the primary element in reactor pressure vessels. Fig. 4 accounts for the several reactions shown in Fig. 2, and folds in the point defect

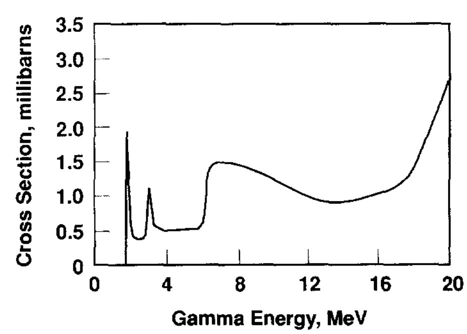

Fig. 3. The (γ, n) reaction cross-section of ^{9}Be as a function of γ-ray energy.

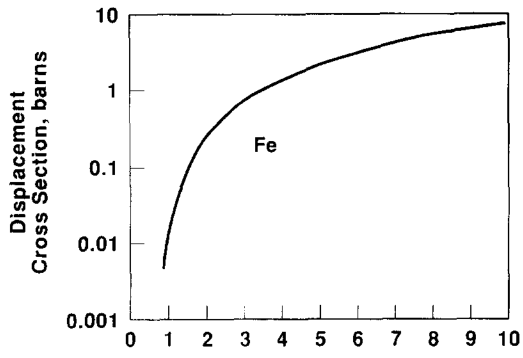

Fig. 4. Displacement cross-section in iron as a function of γ-ray energy, after Ref. [13].

production of each reaction as a function of energy [13]. In the energy range of most interest in reactors (up to a few MeV) the γ displacement cross-section in iron is dominated by Compton scattering [14]. At γ energies in this range, the displacement cross-section is in the neighborhood of 1 b. Comparing with Fig. 1 for fast neutrons ($\sim$ 1,000 b), we can write the inequality

$$\frac{\phi_\gamma}{\phi_f} \geq 100, \tag{9}$$

as the condition for which γ-induced displacements contribute more than 10% compared to fast neutron induced displacements. In the inequality (9), ϕ_γ is the flux of hard γ-rays, say above about 2 MeV. For γ's significantly below this energy, a much larger ratio of γ-flux to fast neutron flux would be required to produce a significant number of displacements relative to those produced by fast neutrons.

4. 'Early' embrittlement of the HFIR reactor vessel

The analysis presented in this paper of possible mechanisms of displacement production was initiated in response to previous work at Oak Ridge National Laboratory on the high flux isotope reactor (HFIR) pressure vessel [15]. In that work, experimental Charpy impact data from the HFIR surveillance program coupons indicated that embrittlement was occurring at fast neutron fluences five to ten times lower than expected. These findings of 'accelerated' or 'early' embrittlement were based on extrapolations of data obtained in test reactors at in-core or near-core positions under fast-spectrum, high-damage-rate conditions.

Fig. 5 summarizes this embrittlement situation. The test reactor data, accumulated at fast neutron fluences ($E > 1$ MeV) above about 2×10^{22} n/m^2 indicate that no embrittlement (as measured by increase in Charpy transition temperature) should be expected when extrapolated downward for fluences below about 6×10^{21} n/m^2. However, actual measurements on Charpy impact specimens irradiated near the HFIR pressure vessel at fluences as low as 1×10^{21} n/m^2 indicated upward shifts in the ductile-to-brittle transition temperature of tens of degrees C.

Several mechanisms to explain this discrepancy were explored. These included the possibility of thermal aging-induced hardening over an approximately 20 year period; enhanced availabilities of point defects to induce clustering and precipitation, either (or both) because of an extremely low damage rate or because of a thermalized neutron spectrum; increased damage from the boron (n, α) reaction described above; and an effect of copper precipitation on hardening [16]. Each of these possibilities was examined by experiments and/or analysis, and each was ruled out.

It is now clear that the 'accelerated' embrittlement of the HFIR vessel is due to uncounted displacements caused by γ-rays. The cause was uncovered in the following way. Because of the unusual embrittlement results and the need to confirm detailed particle transport calculations for regions near the vessel, it was decided to carry out extensive dosimetry at several locations at the HFIR vessel. In the dosimetry experiments, significant discrepancies were found between ^{9}Be and ^{237}Np monitors, on the one hand, and Ni monitors on the other hand. The former indicated apparent fast neutron fluxes about 15 times those indicated by the latter. The discrepancy between these monitors and the Ni monitors was explained when it was realized that the excess reaction products of the Be and Np monitors were accounted for by photonuclear events. The Be and Np monitors undergo photonuclear reactions, (γ, n) for the

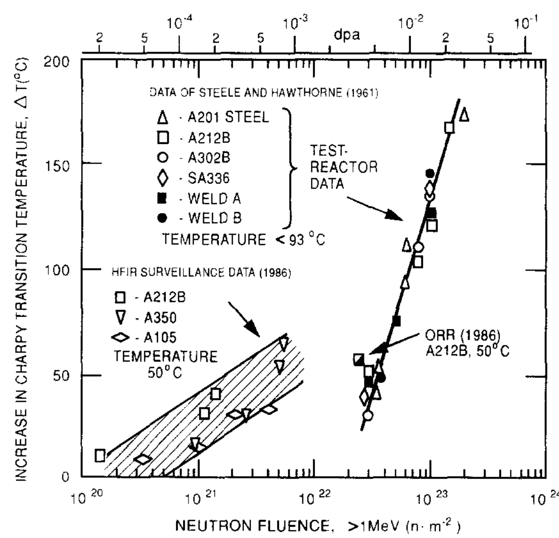

Fig. 5. Charpy transition temperatures in various pressure vessel steels plotted as a function of fast neutron fluence. In this plot the HFIR surveillance data points fall at much lower fluences than data obtained in test reactors.

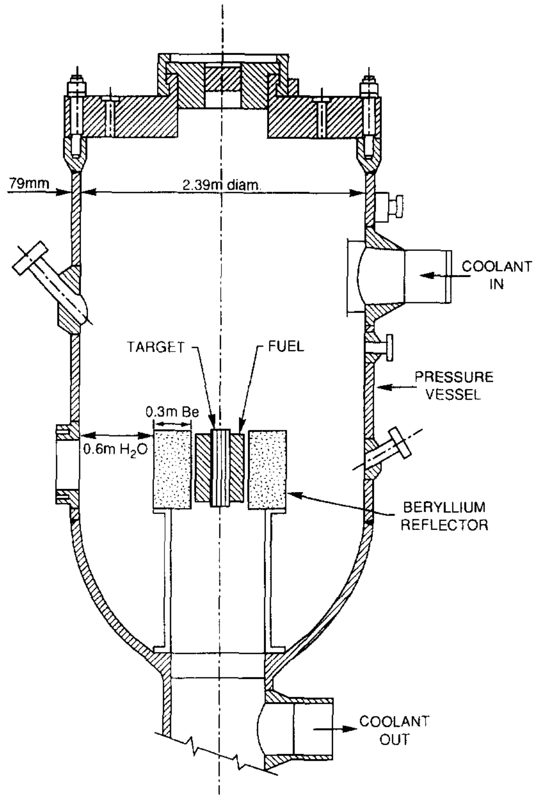

Fig. 6. Simplified vertical cross-section through the core, reflector, water and vessel of the HFIR reactor.

former and (γ, fission) for the latter. These augment the fast neutron reactions in creating reaction products that are measured in the dosimetry experiments. These results were confirmed by additional dosimetry and by transport calculations, which showed that

$$\phi_\gamma / \phi_f \sim 10^4 \tag{10}$$

at the HFIR vessel. Comparing with the inequality (9) we see that the experimentally confirmed result (inequality 10) is sufficient to make the γ-induced displacements not only significant, but in fact the dominant cause of displacements.

The reason for the high ratio of inequality (10) can be seen in Figs. 6 and 7. Fig. 6 is a simplified view of the reactor vessel and core region. It shows that there is a long water path between the core, the Be reflector, and vessel [17]. Fig. 7 shows the attenuation of both neutron and gamma fluxes with distance from the core [18]. It can be seen that the neutrons are attenuated much more effectively than the γ-rays by the water surrounding the core. In the core the gamma flux exceeds the fast neutron flux by only several fold. At the vessel the ratio is about 10^4.

When the additional displacements produced by the γ-rays are accounted for, the apparent discrepancy of Fig. 5 is removed. Fig. 8 (the results of tensile tests that show a similar behavior with respect to dose as the impact tests of Fig. 5) shows that, when the γ-displacements are included, the data points for the HFIR are translated so that they fall on the same curve as the data points from the Oak Ridge research reactor (ORR). The latter were obtained at in-core and near-core positions [15].

The implications of this work are that in reactors with large water paths, the components so exposed may be subject to γ-embrittlement. Fortunately, γ-induced displacements are not expected to be significant with respect to fast neutron displacements in most existing water-cooled

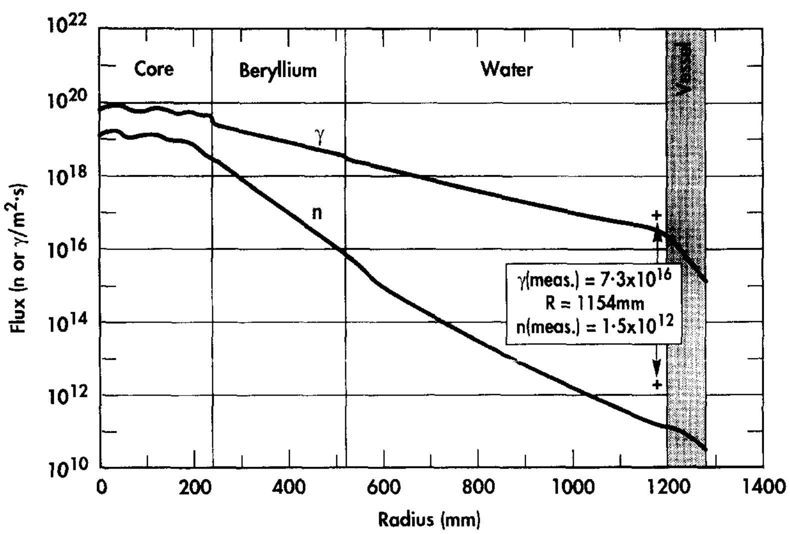

Fig. 7. Fast neutron and hard gamma flux as a function of distance for the center of this HFIR reactor core (for $E_n > 1$ MeV and $E_\gamma > 1$ MeV).

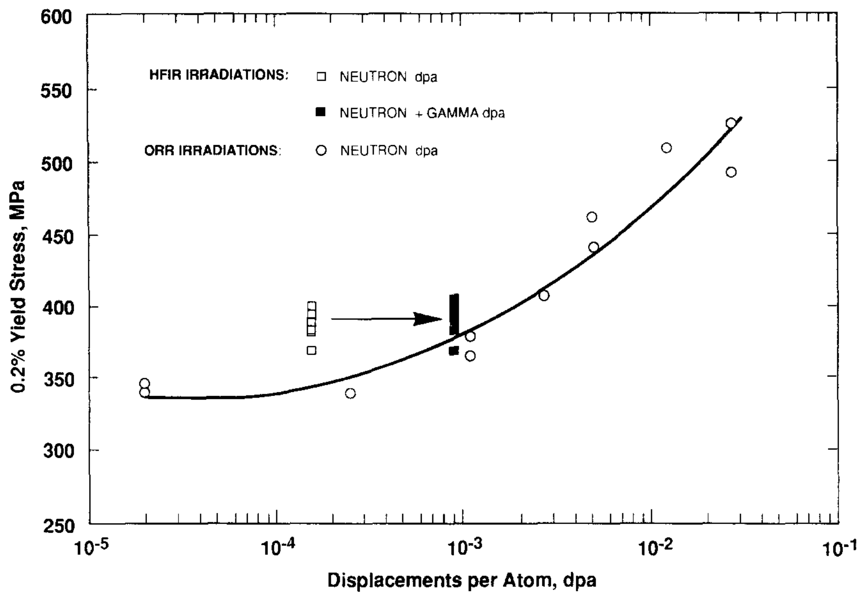

Fig. 8. Yield stress, a measure of hardening and embrittlement, as a function of dose in displacements per atom. When all displacements, including those from γ-rays, and accounted for, the HFIR points fall near the other data.

reactor vessels, because the water paths are not sufficiently long. However, recent calculations [19] show that in the vessel of an advanced boiling water reactor design that incorporates a large water-filled gap, more displacements are predicted from hard γ-rays than from fast neutrons. Fortunately, the large water gap also reduces the overall displacements to a level low enough that embrittlement of the vessel may not be of concern.

5. Summary and conclusions

There are a number of processes, in addition to fast neutron reactions that may cause displacement of atoms. Under certain conditions these may become significant in contributing to the embrittlement of pressure vessel steels. In general, all possible sources of displacement should be evaluated for each material of interest in a given irradiation environment. In this paper several possible energetic events have been evaluated, viz., recoils from thermal neutron (n, γ) reactions, reaction products from thermal (n, α) reactions and photoelectron reactions. Simple expressions are presented in terms of irradiation and material parameters identifying the conditions under which each process would become significant in comparison to displacements induced by fast neutrons. The early embrittlement of the HFIR reactor vessel is explained as a demonstration of the importance of a process other than fast neutron displacements. In that case, high fluxes of γ-rays were found to contribute the dominant source of displacements leading to embrittlement. This new discovery in a research reactor suggests that other situations where the environment contains hard γ-rays and long water paths should be examined for an increased relative importance of γ-induced damage. The present approach may be used to identify other situations where embrittlement rates and radiation effects from other sources, such as those examined here, may exceed conventional estimates based on fast neutron fluences alone.

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