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Modeling of Radiation Hardening
Due to Point Defect Clusters in Stainless Steels

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Abstract

A model is presented that estimates the amount of radiation hardening under neutron irradiation. A reaction rate theory was employed to describe the evolution of microstructure in stainless steel leading to radiation hardening. The model assumes that point defect clusters (interstitial- and vacancy-type) are the primary sources of hardening and these defects eventually act as barriers to the dislocation motion. Small clusters can be created directly from the displacement cascade and be developed by diffusive mechanism between mobile point defects and clusters. Based on the model, we computed PDC distributions numerically and estimated the increase in yield strength. Both types of clusters can give rise to significant hardening. The effect of displacement rate has been investigated using the PDC model calculation. It could be found that higher displacement rate can lead to more hardening.

1. Introduction

One of the most important issues in the nuclear industry is to assess the performance and integrity of structural materials in the light water reactors. Changes in microstructure under neutron irradiation bring about the mechanical property changes of materials. Among several changes, the major concern in this study is radiation hardening, which is generally expressed in terms of an increase in yield strength as a function of radiation dose and temperature. A number of models have been developed to describe the microstructural evolution under irradiation. Empirical models have been proposed to investigate embrittlement of reactor pressure-vessel (RPV) steel.[1,2] These models assume that changes in yield strength arise from the combined effects of defect clusters and copper precipitates, resulting from irradiation. The contribution of each effect to yield stress is correlated to the fast neutron fluence and the volume fraction of copper. Based on the reaction rate theory, the theoretical model has been developed to describe the evolution of point defect clusters (PDC).[3,4] These defects are believed to be major sources of hardening in steels used for light water reactor components.

Development of theoretical models is limited due to the incomplete kinetic data and large heat-to-heat variations in microstructural data. These variations are related to such irradiation conditions as temperature, flux, and fluence at which the experiment was conducted. Also, subtle changes in minor alloying elements and details of thermomechanical treatment affect significantly the apparent property changes. Such sensitivity increases the uncertainty in determining kinetic parameters depending on alloys, which include diffusion coefficients, point defect migration and formation energies, *etc*. However, theoretical approaches may provide an expedient tool in predicting the mechanical property changes of irradiated materials, as well as interpreting the experimental data.

The model below was developed by Stoller to investigate and describe the microstructural evolution of ferritic steels under irradiation.[3] This model consists of two parts. First, the formation of two types of PDC (interstitial and vacancy) is described mathematically using the reaction rate theory. The concentration of PDC and its size are obtained from computation. Then, we apply the dislocation barrier model to predict the changes in yield strength of irradiated alloys. In this study, the emphasis is placed on the increase in yields strength of irradiated stainless steels 304 and 304L. Due to the lack of information on material and irradiation parameters of stainless steels, we used published data through literature review. The major approximation here is in the use of material parameters of the interstitial migration energy.

2. Model Description

Low temperature (< 300^{o}C) irradiation of stainless steels produces primarily small dislocation loops and defect clusters, which will provide effective barriers to dislocation movement, increasing the yield strength.[5] The time-dependent behavior of interstitial and vacancy clusters by solid sate diffusion and interaction with sinks can be estimated using the PDC model developed by Stoller.[3] Details of models will be explained in this section by dividing three parts.

2.1 Point Defect Kinetics Model

The point defect concentrations for interstitial (C_i) and vacancy (C_v) are given by:

$$\frac{dC_i}{dt} = P_i - R_{iv} C_i C_v - D_i \sum_j S_{ji} C_i \qquad (1)$$

$$\frac{dC_v}{dt} = P_v - R_{iv} C_i C_v - D_v \sum_j S_{jv} C_v \qquad (2)$$

where P_i and P_v are the interstitial and vacancy production rates, R_{iv} is the recombination constant, the D_i and D_v are the diffusion coefficients for each point defect, and the S_{jx} are the sink strengths for the absorption of point defect x (i or v) by sink type j. The sinks included in this model are network dislocations, grain boundaries, and irradiation induced point defect clusters.

The interstitial production rate, P_i in Eq. (1), consists of two factors; Migrating point defects from neutron irradiation, and mobile single interstitials emitted from small size (up to four) interstitial clusters. Although single interstitials can be generated by emission from other sinks, this process is neglected since the interstitial formation energy is so high (about 4 eV) and irradiation temperature of interest (< 300 ^{o}C) is sufficiently low that it is not probable that single interstitials can be ejected from higher order interstitial clusters. Generally, the point defect production rate is different from displacement per atom (dpa) rate in that the dpa value does not take into account the effect of cascade efficiency and in-cascade clustering fraction. Therefore, when accounting for theses two factors, the point defect production rates should be reduced significantly. Under these assumptions, P_i can be written as;

$$P_i = G_{dpa}\,\eta\,(1 - f_{icl}) + \sum_{j=2}^{4} E_i^j\, C_j \tag{3}$$

where, G_{dpa} is the *dpa* rate, which can be readily obtained from the SPECTER code calculation for given neutron spectrum,[6] η is the cascade efficiency, and f_{icl} is the fraction of the primary interstitials that participate in the clustering formation. And, the E_i^j are the rate constants for interstitial emission from a j-interstitial cluster and C_j represents the concentration of a j-interstitial cluster. In a similar way, the vacancy production rate, P_v, is given as:

$$P_v = G_{dpa}\,\eta\,(1 - f_{vcl}) + D_v C_v^e \sum_j S_{jv} \tag{4}$$

where C_v^e is the thermal equilibrium vacancy concentration and the S_{jv} are the vacancy sink strengths for the extended defects of type j. Such extended defects can act as sources of point defects, as well as sinks for point defects in austenitic steels. In the present model, the sink structure includes network dislocation, grain boundary, and PDC.

The strength of the various sinks in the microstructure varies with irradiation. The sinks present before irradiation include network dislocations, precipitates, and interfaces. The strength of other sinks such as PDC, dislocation loops, and voids can grow and increase in density as irradiation proceeds. It is assumed that two types of sinks, network dislocations and grain boundaries, do not change in size and strength with irradiation. On the other hand, point defect clusters are regarded as time-dependent sinks which change in size and number density during irradiation. The sink strengths of network dislocations for interstitial and vacancy are

$$S_{i,v}^{dis} = z_{i,v}^{dis}\,\rho_{dis} \tag{5}$$

where ρ_{dis} is the dislocation density in units of cm^{-2} and $z_{i,v}^{dis}$ are the dislocation bias factors for interstitial and vacancy.[7] The grain boundary sink strength is expressed as:

$$S_{gb} = \frac{6\sqrt{S_o^T}}{d_g} \tag{6}$$

where S_o^T represents the vacancy sink strength of internal sinks such as voids and dislocations and d_g is the effective grain diameter. Eq. (6) implies the assumption that the total sink strength of grain boundaries for interstitial is not different from that for vacancy. In addition to the pre-existing sinks, point defect clusters that develop during irradiation are sinks for mobile point defects themselves. If the vacancy cluster is assumed to take the form of a microvoid, then its sink strength is given as:

$$S_{i,v}^{vcl} = 4\pi\, r_{vcl}\, N_{vcl} \tag{7}$$

where r_{vcl} is the radius of the vacancy cluster and N_{vcl} its number density in units of $\#/cm^3$. The interstitial cluster is considered to be a planar defect, or a dislocation loop. The interstitial cluster sink strength is, then, expressed in terms of combinatorial numbers $\delta_{i,v}^j$, determined by the number of neighboring atomic sites from which a vacancy or interstitial can jump onto a j-size interstitial cluster. The sink strength of the interstitial cluster is written as:

$$S_{i,v}^{icl} = \sum_j \frac{\delta_{i,v}^{j}}{a_L^2} C_j \tag{8}$$

where a_L is the lattice constant. The PDC sinks, $S_{i,v}^{vcl}$ and $S_{i,v}^{icl}$, should be determined by coupling with the equations for PDC model described in the next section. Then, the total sink strength shown in Eqs. (1) and (2) can be obtained by summation of Eqs. (5) to (8).

2.2 Point Defect Clustering Model

The basic mechanism of PDC evolution is nucleation and growth by diffusive reactions between PDC and point defects. The evolution of PDC begins with the formation of small size clusters created directly by neutron displacement cascades. It is important to note that nucleation of PDC takes place in the displacement cascades. These defect clusters will grow in size and density as irradiation proceeds. In order to quantify the fraction of point defect clustering from displacement cascades, we use results obtained from molecular dynamics (MD) simulations.[8,9] There are two important parameters required for the quantification of PDC nucleation: the cascade efficiency η and the in-cascade clustering fraction f_{cl}. The cascade efficiency η represents the fraction of defects which escape from in-cascade recombination, and the in-cascade clustering fraction f_{cl} is the fraction of the remaining displacements that forms PDC. Both the cascade efficiency and the clustering fractions depend on the energy of the primary knock-on atom (PKA) that brings about the cascade. We used several values of η and f_{cl} to fit the calculation results to the observed data on yield strength of irradiated SS 304(L).

The evolution of interstitial cluster population is expressed in terms of a set of time-dependent ordinary differential equations describing the balance of point defect clusters as they are created and absorb or emit vacancies or interstitials, thereby changing size and density. The basic assumption in this model is that neutron irradiation creates interstitial clusters of up to four interstitials and these can grow to clusters containing up to 500 interstitials. The rate equations for the description of the interstitial clusters are:

$$\frac{dC_2}{dt} = \eta G_{dpa} \frac{f_{icl}^2}{2} + \beta_i^1 \frac{C_i}{2} + \left(\beta_v^3 + E_i^3\right)C_3 - \left(\beta_v^2 + \beta_i^2 + E_i^2\right)C_2 \quad \text{for di-interstitials} \tag{9}$$

$$\frac{dC_3}{dt} = \eta G_{dpa} \frac{f_{icl}^3}{3} + \beta_i^2 C_2 + \left(\beta_v^4 + E_i^4\right)C_4 - \left(\beta_v^3 + \beta_i^3 + E_i^3\right)C_3 \quad \text{for tri-interstitials} \tag{10}$$

$$\frac{dC_4}{dt} = \eta G_{dpa} \frac{f_{icl}^4}{4} + \beta_i^3 C_3 + \beta_v^5 C_5 - \left(\beta_v^4 + \beta_i^4 + E_i^4\right) C_4 \quad \text{for tetra-interstitials} \tag{11}$$

$$\frac{dC_5}{dt} = \beta_i^4 C_4 + \beta_v^6 C_6 - \left(\beta_v^5 + \beta_i^5\right) C_5 \quad \text{for penta-interstitials} \tag{12}$$

$$\vdots \qquad \vdots \qquad \vdots$$

$$\frac{dC_m}{dt} = \beta_i^{m-1} C_{m-1} + \beta_v^{m+1} C_{m+1} - \left(\beta_v^m + \beta_i^m\right) C_m \quad \text{for } 6 \le m \le 500 \tag{13}$$

where C_m is the concentration of an m-interstitial cluster (atomic fraction), f_{icl}^{m} the fraction of the defects created by the cascade that are in an m-interstitial cluster, and G_{dpa} the *dpa* rate (dpa/s) produced by neutron irradiation. The rate constants $\beta_{i,v}^{m}$ are the probability of absorption of a mobile interstitial or vacancy into an m-interstitial cluster per unit time. This is written as:

$$\beta_{i,v}^{m} = \frac{\delta_{i,v}^{m}}{a_L^2} C_{i,v} D_{i,v} \tag{14}$$

The rate constants E_i^u are the probabilities of the emission of a single interstitial from a u-interstitial cluster per unit time, expressed as:

$$E_i^u = \frac{D_i}{a_L^2} \exp\left(-\frac{E_u^B}{kT}\right) \qquad \text{for } 2 \le u \le 4 \tag{15}$$

where k is the Boltzmann constant, T is the irradiation temperature, and E_u^B the binding energy of an interstitial to a u-interstitial cluster. As stated previously, interstitial emission from larger clusters (greater than tetra-interstitial) is not taken into account because of the relatively higher binding energy of larger clusters.

The development of vacancy clusters is described by a simple creation and decay model. At low temperature ($< 300\ ^{o}$C), it is unlikely that vacancy clusters grow and become voids. The vacancy clusters are assumed to form in the displacement cascade as microvoid with a constant radius and to change in size depending on the balance of the relevant point defect fluxes. In this model, we assume that vacancy clusters corresponding to 10 vacancies are created directly from the displacement cascade. The rate of change in the radius of a vacancy cluster is given as:

$$\frac{dr_{vcl}}{dt} = \frac{1}{r_{vcl}}\left(D_v C_v - D_i C_i - D_v C_v^{vcl}\right) \tag{16}$$

where r_{vcl} is the size (radius) of a vacancy cluster and C_v^{vcl} is the vacancy concentration in the matrix in equilibrium with the microvoid. The C_v^{vcl} in Eq. (16) can be expressed as:

$$C_v^{vcl} = C_v^{e} \exp\left(\frac{2\gamma_s \Omega}{r_{vcl} kT}\right) \tag{17}$$

where γ_s is the surface energy and Ω the atomic volume. In the fcc lattice, the atomic volume is defined as $a_L^3/4$. Then, the rate of change in the concentration of vacancy cluster N_{vcl} is given as a function of vacancy cluster production rate G_{vcl} and its mean lifetime τ_{vcl}.

$$\frac{dN_{vcl}}{dt} = G_{vcl} - \frac{N_{vcl}}{\tau_{vcl}} \tag{18}$$

The vacancy cluster production rate, G_{vcl} in Eq. (18), is given by:

$$G_{vcl} = \eta \, f_{vcl} \, \frac{G_{dpa}}{\Omega \, n_v} \tag{19}$$

where, n_v is the number of vacancies per cluster created in a displacement cascade. The mean lifetime of a vacancy cluster, τ_{vcl} in Eq. (18), is calculated by integrating Eq. (16)

$$\tau_{vcl} = \int_{r_i}^{r_1} \frac{dr_{vcl}}{(dr_{vcl} / dt)} \tag{20}$$

where r_1 is the radius of single vacancy and r_i the initial radius of vacancy cluster, which is determined by n_v.

These equations for point defect clusters, as well as point defect kinetics, are solved simultaneously using the FORTRAN subroutine *dlsode*, designed to solve stiff-and/or nonstiff-type ordinary differential equations.[10]

2.3 Radiation Hardening due to PDC

Radiation hardening can be estimated using the dislocation barrier model which describe the interaction forces of various defects as they impede the mobile dislocation motion along the slip planes of the material. Such models are based on Orowan' s theory for the bending of dislocations around precipitates.[11] A change in shear stress $\Delta\tau$ due to such defects is expressed as:

$$\Delta\tau = \frac{\mu \, b}{\chi \, \lambda} \tag{21}$$

where μ is the shear modulus, b is the Burgers vector, χ is a factor inversely proportional to the barrier strength, and λ is the average inter-barrier spacing. The average barrier spacing, λ is determined by the size d_n and concentration N_n of barriers and is given by:

$$\lambda = \left(\sum_n d_n \, N_n \right)^{-\frac{1}{2}} \tag{22}$$

As a result of the PDC model calculations, we can obtain the size and concentration of PDC, required to calculate the average spacing in Eq. (22). The basic idea of Eq. (22) is that under an applied stress, the dislocation breaks through the barriers and advances on the slip plane until another barrier is encountered. The stress required to move dislocations through barriers is related to the strength of the barriers. Its strength is expressed in terms of the parameter χ which determines the degree of hardening depending on the types of barrier. Although there are differences and uncertainties about the determination of χ, PDC in austenitic steels are considered to be weak barriers.[12] The Taylor factor of 3 is used to convert the shear stress to a change in the uniaxial yield strength $\Delta\sigma_{ys}$:

$$\Delta\sigma_{ys} \cong 3 \; \Delta\tau \tag{23}$$

The contribution from different types of defects is taken into account by a superposition relationship under the assumption that interstitial and vacancy clusters are treated as short-range barriers. The total hardening due to PDC is given as:

$$\Delta\sigma_{ys}^{TOT} = \sqrt{(\Delta\sigma_{ys}^{icl})^2 + (\Delta\sigma_{ys}^{vcl})^2} \quad (24)$$

where $\Delta\sigma_{ys}^{icl}$ and $\Delta\sigma_{ys}^{vcl}$ are the change in yield strength from interstitial and vacancy clusters, respectively.

3. Calculation Results

There exists a degree of uncertainty in determining kinetic and material parameters including interstitial migration energy, point defect clustering fraction, etc. The effect of such uncertainty on results was investigated by performing a parametric study in which we varied parameters for the given ranges. The kinetic and material parameters were optimized to attain reasonable results from PDC calculations by comparing the measured yield strength of irradiated stainless steels. The values listed in Table 1 provide the best estimates for austenitic steels. Another factor that affects the degree of hardening is the parameter of χ in Eq. (21). We referred to Ref. [12] for the determination of barrier strength, which are assigned to 5 and 4 for interstitial and vacancy clusters, respectively.

Figure 1 shows the behavior of point defect concentrations at 288^{o}C as a function of irradiation time, obtained using parameters given in Table 1. The interstitial concentration

Table 1 Kinetic and material parameters for stainless steels 304(L)

Parameters	Values
Irradiation temperature (T)	561 K
Vacancy migration energy (E_v^m)	1.4 eV
Vacancy formation energy (E_v^f)	1.5 eV
Effective grain diameter (d_g)	0.0001 cm
Interstitial migration energy (E_i^m)	0.65 eV
Interstitial pre-exponential factor	0.0659 cm^2/sec
Vacancy pre-exponential factor	0.659 cm^2/sec
Dislocation interstitial bias (z_i^{dis})	1.25
Dislocation vacancy bias (z_v^{dis})	1
Lattice constant (a_L)	3.68 x 10^{-8} cm
Dislocation density (ρ_{dis})	5 x 10^{10} cm^{-2}
Vacancy clustering fraction (f_{vcl})	0.3
Interstitial clustering fraction ($f_{icl}^2 : f_{icl}^3 : f_{icl}^4$)	0.15 : 0.1 : 0.05
Interstitial cluster binding energy ($E_2^B : E_3^B : E_4^B$)	0.75 : 1.0 : 1.25 eV
Initial number of vacancies per vacancy cluster (n_v)	10
Surface energy (γ_s)	2.26 - 8.75 x 10^{-4} T(K) J/m^2
Burgers vector (b)	2.07 x 10^{-8} cm
Shear modulus (μ)	7.6 x 10^4 MPa

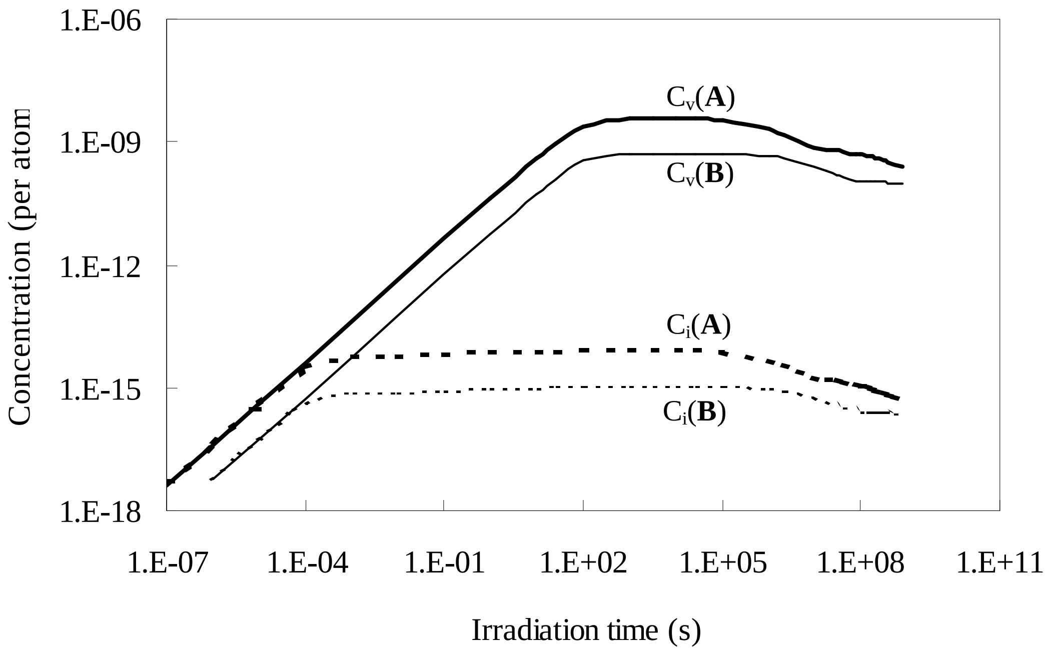

Figure 1. Time dependence of the interstitial (i) and vacancy (v) concentrations at 288°C for given *dpa* rates (**A**: 1.23x10^{-9}, **B**: 1.91x10^{-10} /s)

reaches quasi-steady state essentially instantaneously (at about 10^{-3} seconds) and remains mostly constant, for about 10^{5} seconds. The vacancy concentration reaches quasi-steady state at about 10^{2} seconds. During this quasi-steady state period between 10^{2} and 10^{5} seconds, the point defects are absorbed mainly to pre-existing sinks such as network dislocations and grain boundaries. The contribution of developing sinks to point defect transient starts to take effect from about 10^{5} seconds on. The formation of irradiation-induced PDC leads to the decrease in the point defect concentrations since defect clusters play a significant role in absorbing point defects.

The time dependence of interstitial cluster concentrations is shown in Figure 2, where three types of interstitial clusters are included. Concentrations of smaller size clusters are much higher than those of larger clusters at an early time. This is because the small interstitial clusters (up to tetra-interstitials) are assumed to be created directly by neutron irradiation. Although higher-order interstitial clusters appear to be constant as irradiation proceeds, in fact they gradually increase with time in a small amount. Figure 3 shows the number density of vacancy clusters as a function of time for given *dpa* rate rates. The vacancy cluster concentration reaches a saturation value as irradiation time approaches its lifetime. Lower *dpa* rate gives rise to a longer lifetime of the vacancy clusters.

The estimated value of increase in yield strength for two different displacement rates is plotted in Figure 4. In this calculation, we assume that the vacancy cluster is more effective in hindering the dislocation motion rather than the interstitial cluster. It is seen that higher *dpa* rate can lead to more hardening, which is related to the potential effect of neutron flux on radiation hardening. That is, the amount of radiation hardening increases with fast neutron flux at the same total fluence.

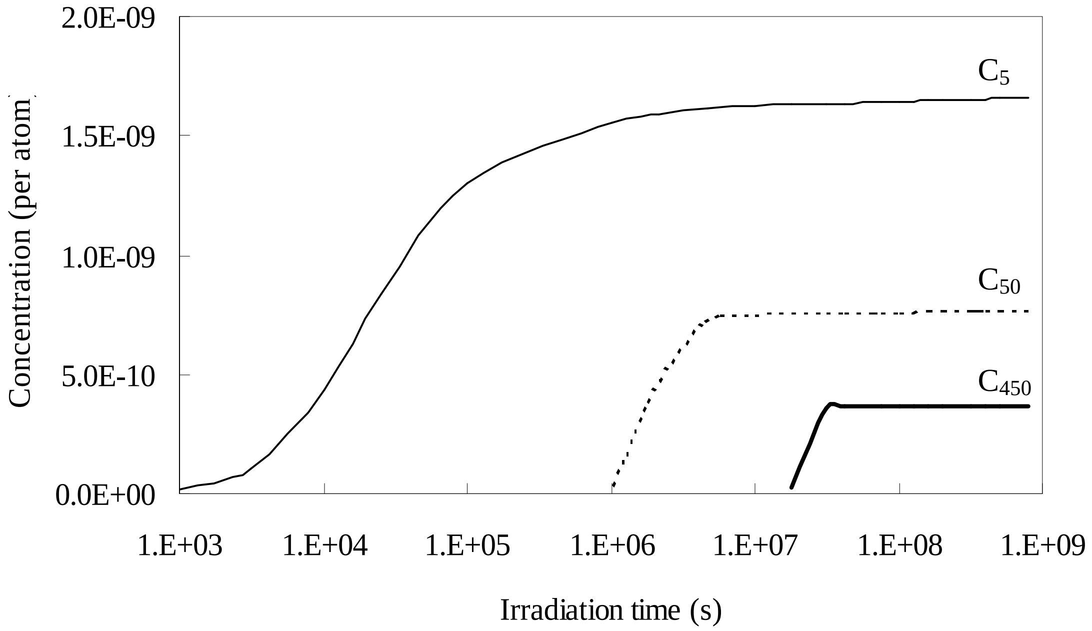

Figure 2. Time dependence of interstitial cluster (5-, 50-, 450-interstitial) concentration at 288°C for *dpa* rate of 1.23x10^{-9} /s.

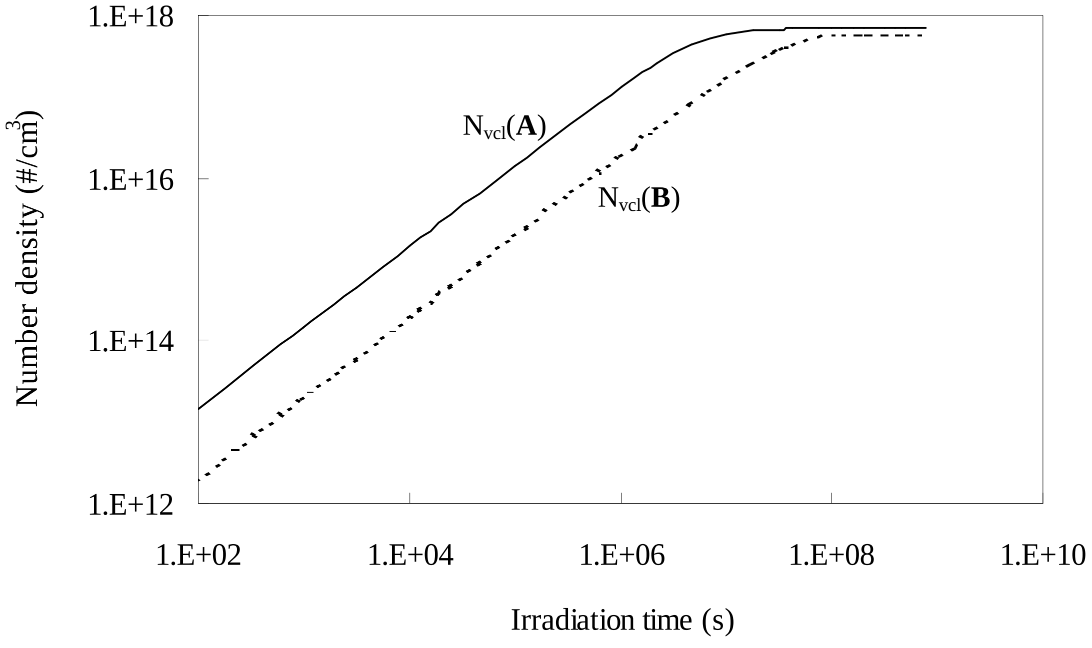

Figure 3. Changes in vacancy cluster concentration as a function of irradiation time at 288°C for given *dpa* rates (**A**: 1.23x10^{-9}, **B**: 1.91x10^{-10} /s)

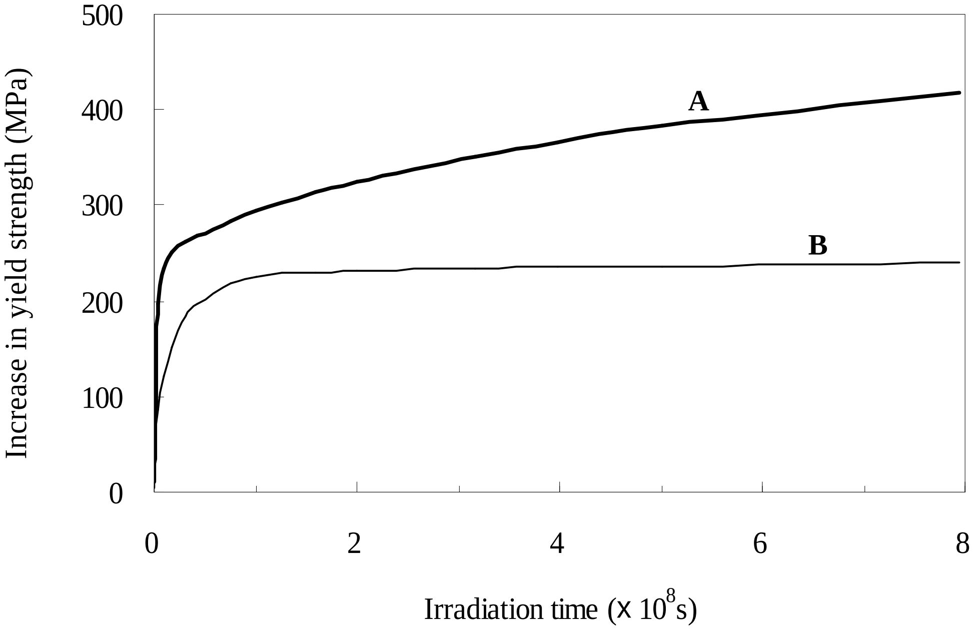

Figure 4. Estimated increase in the yield strength of stainless steel 304 at 288°C for given *dpa* rates (**A**: 1.23×10^{-9}, **B**: 1.91×10^{-10} /s), resulting from the PDC model calculation.

4. Discussion

The time-dependent model has been used to describe the contribution of interstitial and vacancy clusters to radiation hardening in stainless steels. It appears that the cluster contribution to radiation hardening from this model is overestimated since the model does not include other types of microstructure except point defect clusters. However, it is reasonable to conclude that these clusters are responsible for hardening in that the identities of microstructure evolved from irradiation are not still clear.

Although there is some uncertainty in determining the kinetic and material parameters for stainless steels and the strength of point defect clusters as barriers to dislocation motion, we established a theoretical and mathematical way for the estimation of radiation hardening. This mathematical model can be readily applicable to other alloys, such as ferritic steels, for predicting embrittlement. Some modification can be made to this model by including the formation of copper-rich precipitates in RPV steels. Among various parameters listed in Table 1, parameters concerning the clustering formation are closely related to the primary damage production by irradiation. Molecular dynamics calculation will be performed to simulate the primary damage. Results will provide the reliable input to the PDC model calculation.

5. Acknowledgments

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