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Reaction kinetic analysis of reactor surveillance data

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ABSTRACT

In reactor pressure vessel surveillance data, it was found that the concentration of matrix defects was very low even after nearly 40 years of operation, though a large number of precipitates existed. In this paper, defect structures obtained from surveillance data of A533B (high Cu concentration) were simulated using reaction kinetic analysis with 11 rate equations. The coefficients used in the equations were quite different from those obtained by fitting a Fe-0.6 wt%Cu alloy irradiated by the Kyoto University Reactor. The difference was mainly caused by alloying elements in A533B, and the effect of alloying elements was extracted. The same code was applied to low-Cu A533B irradiated with high irradiation damage rate, and the formation of voids was correctly simulated.

1. Introduction

High-energy particle irradiation induces damage in solids and changes their properties. In particular, the degradation of mechanical properties of structural materials used in nuclear power plants is of critical importance. Neutron irradiation embrittlement of reactor pressure vessel steels is one of the principal aging issues. The number of reactors worldwide that have been in operation for about or more than 40 years is increasing. Surveillance data from these aged reactors indicate higher ductile brittle transition temperatures than those predicted by embrittlement correlation methods [1,2]. In particular, the precipitates are the main defect clusters, and only small quantities of loops were observed by transmission electron microscopy. No evidence of vacancy clusters was detected [3]. Table 1 shows an example of surveillance data of the Genkai Unit 1 from Kyushu Electric Power Co., Inc. [4,5]. This unit is a pressurized water reactor and the first unit is in operation since 1975. The pressure vessel is a low alloy steel A533B (Mn: 1.48, Ni: 0.56, Mo: 0.47, Si: 0.25, Cu: 0.12, P: 0.010, S: 0.014 wt%). The nature of the loops was not mentioned, but it should be of interstitial type.

The defect structural evolution of pressure vessel model alloys (Fe-0.6 wt%Cu), irradiated by Kyoto University Reactor (at 573 K, with 1.5×10^{-8}dpa/s) were analyzed using reaction kinetic analysis [6]. Experimental results of defect structural evolution in Fe-0.6 wt%Cu were correctly reproduced by simulations.

In this paper, the defect structural evolution obtained from surveillance data from the Genkai Unit 1 was simulated with the same code adopted in Ref. [6]. It was impossible, however, to simulate the evolution by changing only the damage rate and irradiation temperature, because the surveillance test pieces are made of A533B and contain a lot of alloying elements other than Fe-0.6 wt%Cu. We therefore adjusted the coefficients of the rate equations to reproduce the surveillance data by introducing and analyzing effects due to alloying elements. The code was then applied for analyzing defect structures of low Cu A533B irradiated by the Japan Materials Testing Reactor (JMTR), with a damage rate of 3.3×10^{-7} dpa/s.

2. Method

The model used for the calculations is based on the rate theory and it was also used in a previous paper [6]. The model describes the reaction rates among point defects and their defect clusters [7]. The following assumptions were made in the calculation:

(1) The time dependence of 11 variables is calculated near 1 dpa for the following quantities: the concentration of interstitials, interstitial clusters (interstitial-type dislocation loops), vacancies, vacancy clusters in the matrix (voids), solutes, solute–vacancy pairs, solute–vacancy clusters, the total interstitials in interstitial type dislocation loops, the total vacancies in voids, the total vacancies in solute–vacancy

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clusters, and the total solute atoms in solute–vacancy clusters. The average cluster size is considered.
(2) Mobile defects are interstitials, vacancies, and solute–vacancy pairs.
(3) The thermal dissociation of vacancies is considered for solute–vacancy pairs, voids and vacancies in solute–vacancy clusters. After the dissociation of all vacancies, solute–vacancy clusters are considered as precipitates.
(4) Di-interstitials and di-vacancies are set for stable nuclei belonging to loops and voids, respectively [8,9].
(5) Vacancy + solute–vacancy pair, solute–vacancy pair + solute–vacancy pair, and solute + solute–vacancy pair are also set for stable nuclei of solute–vacancy clusters.

The concentrations of interstitials (C_I), vacancies (C_V), isolated solutes in the matrix (C_M), and solute–vacancy pairs (C_{VM}) are expressed as:

$$\frac{dC_I}{dt} = P_I - 2Z_{I,I}M_IC_I^2 - Z_{I,V}(M_I+M_V)C_IC_V - Z_{I,VM}M_IC_IC_{VM} - Z_{I,IC}M_IC_IS_{IC} - Z_{I,VC}M_IC_IS_{VC} - Z_{I,PC}M_IC_IS_{PC} - M_IC_IC_S - N_IP_{IC}$$

$$\frac{dC_V}{dt} = P_V - 2Z_{V,V}M_VC_V^2 - Z_{I,V}(M_I+M_V)C_IC_V - Z_{V,VM}(M_V+M_{VM})C_VC_{VM} - Z_{V,VC}M_VC_VS_{VC} - Z_{V,IC}M_VC_VS_{IC} - Z_{V,PC}M_VC_VS_{PC} - Z_{V,M}M_VC_VC_M + B_{V,M}M_VC_{VM} + B_{V,PC}M_VS_{PC} + B_{V,VC}M_VS_{VC} - M_VC_VC_S - N_VP_{VC}$$

$$\frac{dC_M}{dt} = Z_{I,VM}C_IC_{VM} + B_{V,VM}M_VC_{VM} - Z_{VM,M}M_{VM}C_{VM}C_M - Z_{V,M}M_VC_VC_M$$

$$\frac{dC_{VM}}{dt} = -Z_{I,VM}C_IC_{VM} - Z_{V,VM}(M_V+M_{VM})C_VC_{VM} - 2Z_{VM,VM}M_{VM}C_{VM}C_{VM} - Z_{VM,M}M_{VM}C_{VM}C_M - B_{V,VM}M_VC_{VM} - Z_{VM,IC}M_{VM}C_{VM}S_{IC} - Z_{VM,VC}M_{VM}C_{VM}S_{VC} - Z_{VM,PC}M_{VM}C_{VM}S_{PC} - M_{VM}C_{VM}C_S,$$

where P is the production rate of point defects (damage rate) and Z is the number of sites in the spontaneous reaction for each process. M is the mobility of defects, and it is expressed as $\nu\exp(-\frac{E_M}{kT})$, where ν is an effective frequency associated with the vibration of the defects in the direction of the saddle point, and it is taken as 10^{13}/s. E, k, and T are the migration energy, the Boltzmann constant and the temperature, respectively. N is the number of atoms in the clusters formed directly in cascade processes. B is the dissociation probability of vacancies with solute–vacancy pairs, voids and solute–vacancy clusters, and it is expressed as $\exp(-\frac{K}{kT})$, where K is the binding energy. $K_{V,M}$, $K_{V,VC}$, and $K_{V,PC}$ are the binding energies between vacancies and solutes atoms, between vacancies and voids in the matrix, and between vacancies and solute–vacancy clusters, respectively. The subscripts I, V, M, VM, PC, IC, and VC denote interstitials, vacancies, solutes, solute–vacancy pairs, solute–vacancy clusters, interstitial type dislocation loops and voids, respectively. The surfaces, grain boundaries, and pre-existing defects such as dislocations are expressed by the sink efficiency C_S. The concentrations are in fractional units. S is the total sink efficiency of clusters [8,9], expressed as:

$$S_{VC} = \left(48\pi^2 R_{VC}C_{VC}^2\right)^{1/3},$$

$$S_{IC} = 2(\pi R_{IC}C_{IC})^{1/2},$$

$$S_{PC} = \left(48\pi^2 (R_{PV}+R_{PM})C_{PC}^2\right)^{1/3}.$$

The nucleation rates of interstitial type dislocation loops (concentration: C_{IC}), voids (C_{VC}), and solute–vacancy clusters (C_{PC}) are:

$$\frac{dC_{IC}}{dt} = P_{IC} + Z_{I,I}M_IC_I^2,$$

$$\frac{dC_{VC}}{dt} = P_{VC} + Z_{V,V}M_VC_V^2,$$

$$\frac{dC_{PC}}{dt} = Z_{V,VM}(M_V+M_{VM})C_VC_{VM} + Z_{VM,VM}C_{VM}^2 + Z_{VM,M}M_{VM}C_{VM}C_M.$$

P_{IC} and P_{VC} are the production rates of interstitial type dislocation loops and voids directly from cascades, respectively.

The total accumulation of interstitials in loops (R_{IC}), vacancies in voids from the matrix (R_{VC}), and vacancies from solute–vacancy clusters (R_{PV}) are, respectively,

$$\frac{dR_{IC}}{dt} = 2Z_{I,I}M_IC_I^2 + Z_{I,IC}M_IC_IS_{IC} - Z_{VM,IC}M_{VM}C_{VM}S_{IC} - Z_{V,IC}M_VC_VS_{IC} + N_IP_{IC}$$

$$\frac{dR_{VC}}{dt} = 2Z_{V,V}M_VC_V^2 + Z_{V,VC}M_VC_VS_{VC} + Z_{VM,VC}M_{VM}C_{VM}S_{VC} - Z_{I,VC}M_IC_IS_{VC} - B_{V,VC}M_VS_{VC} + N_VP_{VC},$$

$$\frac{dR_{PV}}{dt} = 2Z_{V,VM}(M_V+M_{VM})C_VC_{VM} + 2Z_{VM,VM}M_{VM}C_{VM}^2 + Z_{VM,M}M_{VM}C_{VM}C_M + Z_{VM,PC}M_{VM}C_{VM}S_{PC} - Z_{I,PC}M_IC_IS_{PC} + Z_{V,PC}M_VC_VS_{PC} - B_{V,PC}M_VS_{PC}.$$

The total accumulation of solutes in solute–vacancy clusters (R_{PM}) is

$$\frac{dR_{PM}}{dt} = Z_{V,VM}(M_V+M_{VM})C_VC_{VM} + 2Z_{VM,VM}M_{VM}C_{VM}^2 + 2Z_{VM,M}M_{VM}C_{VM}C_M + Z_{VM,PC}M_{VM}C_{VM}S_{PC}.$$

3. Simulation of surveillance data

The defect structural development of surveillance test pieces obtained by changing the damage rate (from 1.5×10^{-8} dpa/s to 1.3×10^{-10} dpa/s), the temperature (from 573 K to 561 K), and the solute concentration (from 0.6 wt% to 0.68 wt%) of the previous code [6] is shown in Fig. 1. The solute concentration of the surveillance pieces was taken as the sum of the concentrations of Cu and Ni. Both elements are responsible for the embrittlement enhancement of steels [10]. The interaction of Mn with interstitials is important because the Mn–dumbbell binding energy is on the order of 0.4 eV [11–13]. But in the surveillance data of Genkai Unit 1, though the concentration of Mn was three times higher than that of Ni, the precipitation of Mn was much lower than that of Ni [4], and we did not introduce the dumbbell motion of solute-interstitial pairs in our model.

The values of coefficients used are listed in Table 2 under the label "Previous". The simulation predicts correctly vacancy cluster dissolution above 10^{-2} dpa. The decrease of interstitials in the loops around 10^{-4} dpa was caused by the evaporation of vacancies from solute–vacancy clusters [6]. The loop concentration, the number of interstitials in a loop, the precipitate concentration, and the number of solutes in a precipitate are shown in Fig. 2. Above 10^{-4} dpa, vacancies escape from solute–vacancy clusters, which become precipitates. In the same figure, the results of the third and fourth surveillance data are indicated by two large symbols. Loops are observed by transmission electron microscopy with the strain field of dislocations. It is possible to detect loops of 1.5 nm by diffraction contrast images. Therefore the existence of electron microscopically invisible clusters cannot be denied. But in our present study, the main purpose was to explain the defect structure observed in surveillance test pieces, and we did not consider

Table 1
Surveillance data from the Genkai Unit 1, Kyushu Electric Co., Inc. [4,5].

Surveillance number	Irradiation dose (E > 1 MeV)	Loops		Precipitates	
		Concentration	Diameter	Concentration	Diameter
3	3.5×10^{19} n/cm^2	6.6×10^{20} m^{-3}	2.7 nm	2.3×10^{23} m^{-3}	3.0 nm
4	6.5×10^{19}	1.6×10^{21}	3.2	2.5×10^{23}	3.3